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THE ANALYSIS OF METAL FINISHING
SOLUTIONS BY ION CHROMATOGRAPHY

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Ion chromatography is very effective for ionic and polar species determinations. Separation of the analytes into pure peaks simplifies detection compared to detecting the same species in the unseparated sample matrix. One of the methods provides important improvements on existing methods, while the rest provide new and improved ways to analyze metal finishing solutions. The advantages of these methods are that considerable improvements were made in

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20. ABSTRACT (CONT'D)

the areas of: trace ion determinations in the presence of other extremely high ionic concentrations, analysis time, analyst intervention, sensitivity, automation, and multi-ion determinations while maintaining equal precision and specificity compared to traditional chemical methods now in use.

This report describes procedures for the analysis of solutions for chromium plating, acid finishing, metal cyanide plating, and their associated waste solutions. These metal finishing solutions are very successfully analyzed by ion chromatography using a diverse range of techniques.

For the above matrices, the following is a brief summary of the automated procedures developed: analysis of chromium, iron, and copper aqua-complexes using atomic absorption or visible detection; analysis of iron and copper cyano-complexes using atomic absorption or conductivity detection; and analysis of chromate, sulfate, oxalate, phosphate, nitrate, nitrite, formate, and glycolate by conductivity detection. Atomic absorption detection is the laboratory method of choice for metals, while visible and conductivity detection are universally suitable.

An extensive study was made on the influence of injected samples affecting eluent equilibria and thus detection. It is shown that in order to achieve reliable results, samples and standards must have similar acid-base characteristics.

These methods are an improvement to standard methods now in practice and have been tested for three years on real industrial samples with excellent results.

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ABSTRACT

Ion chromatography has become a very efficient means for quantitatively determining ionic and polar species. Detection of a relatively pure chromatographic species peak is a much easier and interference-free procedure compared to detecting the same species in the unseparated sample matrix. Most methods given here provide a new and improved way to analyze metal finishing solutions while a few are important improvements on existing methods. The advantages of these ion chromatographic methods of analysis are that *considerable improvements were made* in the areas of analysis time, analyst intervention, and sensitivity while maintaining equal precision and specificity compared to the traditional wet chemical methods now in use. Additional advantages, compared to the wet chemical methods, are the ability to determine trace ions in the presence of extremely high concentrations of other ions and the capability of automated, multi-ion determinations.

Metal finishing solutions can be quantitatively analyzed by ion chromatography with excellent results. A diverse range of techniques can be applied depending on the analyte and analyte matrix. This report

describes procedures for the analysis of solutions for chromium plating, acid finishing, metal cyanide plating, and their associated waste solutions.

The procedures developed are as follows: analysis of Cr, Fe and Cu aqua-complexes by cationic separation and atomic absorption detection; analysis of Cr, Fe and Cu aqua-complexes by cationic separation, PAR reagent complexing and uv-visible detection; analysis of Cr and Cu EDTA-complexes by anionic separation and uv-visible detection; analysis of Fe and Cu cyano-complexes and free cyanide by MPIC anionic separation and both atomic absorption and suppressed conductivity detection; analysis of chromate, sulfate, phosphate, nitrate, nitrite and oxalate by anionic separation and suppressed conductivity detection; analysis of ethylene glycol degradation products by anionic exclusion separation and suppressed conductivity detection; and automated and online analysis of metal finishing solution ions. The atomic absorption detection methods are the methods of choice for metals in a laboratory situation while the uv-visible and conductivity detectors are suitable for both the laboratory and industrial quality control situations.

An extensive study was made on the influence of injected samples affecting eluent equilibria and thus

detection. It is shown that in order to achieve reliable results, samples and standards must have similar acid-base characteristics.

These methods are an improvement to standard methods now in practice and have been tested for three years on real industrial samples with excellent results.

PART 1

INTRODUCTION AND HISTORICAL REVIEW

Chromatography as a separation technique was invented, developed and named by botonist Dr. Mikhail Tswett, a Russian national, in 1906 when he published a paper on the separation of chlorophylls and other plant pigments (1). In his paper, a column was filled with a dry, solid absorbent of calcium carbonate as the stationary phase and petroleum ether as the mobile phase. Next, plant pigments were extracted with an organic solvent and then a portion of the extract was added to the top of the column. When the column was washed with the mobile phase, the constituents of the extract moved down the column at different rates and resolved themselves into colored rings or bands. The calcium carbonate was removed from the column as an intact cylinder and the bands were cut apart or frationated with a knife. This experiment included all the essential elements of a present day adsorption chromatography method.

The next major analytical development was that of liquid-liquid partition chromatography by biochemists A. Martin and R. Synge in 1941 (2). Instead of only a solid adsorbent, they used a stationary liquid phase

spread over the surface of the adsorbent and immiscible with the mobile phase. The sample components partitioned themselves between the two liquid phases according to their solubilities. Today, Martin and Synge are recognized as developing general chromatographic theory as well as partition chromatography and were honored with the Nobel Prize in chemistry in 1954. In 1942, Martin and Synge suggested that the combination of a gaseous mobile phase with a liquid stationary phase would be very practical for organic analysis.

In 1948, Strain and Moore used a variation of the above partition method called ion exchange chromatography for the separation of amino acids (3).

In 1952, A. Martin and A. James developed gas chromatography which was described by Martin and Synge ten years before. This method is useful for mixtures of gases or for volatile liquids and solids and has become a routine technique due to its high resolution, speed and sensitivity (4).

In 1953, Wheaton and Bauman developed exclusion chromatography for separation of simple components on the basis of molecular weights (5).

It is worth mentioning that in the early 1970's high performance liquid chromatography matured due to

better instrumentation, new column packings, and a better understanding of chromatographic theory. HPLC is useful for rapid separation ot non-volatile and thermally unstable samples (6). In HPLC, instead of using a stationary liquid phase spread over the surface of a solid absorbent, the stationary phase consists of a solid support with chemically bound groups for partitioning. Thus, separation can be achieved at much higher pressures.

In 1975, H. Small, T. Stevens and W. Bauman published the first paper on ion chromatography (7). The column's stationary phase consisted of bound cation groups with the mobile phase eluent consisting of sodium carbonate solution. Anion samples were separated by partitioning; sample anions and eluent carbonate competed for ion exchange sites on the bound cation groups of the solid support. The sodium ions were then replaced with hydrogen ions in the chemical suppressor before conductivity detection. Today, ion chromatography is used for inorganic and organic anions, cations and polar species.

General references on ion chromatography can be found (6-12) to illustrate the broad range that this method covers. In specific areas related to the topic of this report, much work has been done on the analysis

of chromate in aqueous solutions by ion and liquid chromatography (13-20) and there are many r~ferences regarding acid analysis in aqueous solutions by ion and liquid chromatography (21-45). The chromatographic analysis of one ion in the presense of an interfering ion also has been discussed extensively (15, 18, 22, 23, 27-30, 33, 34, 36, 38, 41, 42, 46, 47). The analysis of metals by ion and liquid chromatography using conductivity and ultraviolet-visible detection has been covered (13-16, 18, 19, 45, 48-51). Metals have also been determined offline by indirect atomic absorption detection using ion and liquid chromatography separation (15-17, 20, 32, 52-57). Free cyanide has been determined in metal processing solutions (58, 59).

This report is concerned with the methods of analysis of a variety of metal finishing solutions, where the analytical requirements may be determinations of anions and cations of different elements, the amount of an element in different oxidation states, quantities of free versus complexed species, etc. Specifically, this report describes procedures for the analysis of chromium plating, acid finishing, metal cyanide plating, and their associated waste solutions where the important analytical data are the concentrations

of the ions and metal complexes present, since this information is important for controlling the quality of each metal finishing operation. Particular methods used depend on anion and cation exchange separation; ion-pairing separation; Donnan exclusion separation; ion exclusion separation; metal complexing equlibria; acid-base equlibria; post column reaction and suppression; and atomic absorption, uv-visible and conductivity detection. Very little of the research covered in the works mentioned above has dealt with the analysis of metals in these systems. In addition, some methods that have been described, such as the analysis of anions by ion chromatography, encounter difficulties when samples and standards have different high acid or base concentrations. This matrix problem results from the necessity to simultaneously analyze trace species in the presence of high concentrations of acids or bases and thus dilution is not a practical solution. A final analytical problem addressed here deals with the ability of chromatographic detectors to detect metal complexes at ppm concentration levels either by re-complexing the metal or using very sensitive detection methods.

The following outlines the specific systems that have been explored, and for background, provides a

summary of procedures commonly used in the plating industry for these systems.

The first system to be considered deals with the separation and detection of hexa-aqua Cr(III) and chromate by the use of a cation separator column and atomic absorption detection. Methods were also developed here for the detection of this Cr(III) complex by uv-visible detection. The major applications of this study is for analysis of trivalent chromium in hexavalent chromium plating solutions. No complexing reagents are required and chromate is not retained by the cation separator resin. Only one method appears in the literature using ion chromatography to analyze cations of transition metals (48); but trivalent chromium can not be analyzed by this method.

Trivalent chromium is typically analyzed by first titrating the hexavalent chromium, then oxidizing the trivalent chromium, and retitrating the total chromium. The trivalent chromium is the difference of two large numbers and error is high for this method (60).

A second analytical problem of interest here is the separation and determination of aqua-complexes of Fe(II) and Fe(III), separation of Cu(II) aqua-complexes from Cu(I) cyanide complexes, and other

aspects of the analysis of cyanide plating solutions. The presence of iron, as well as the overall distribution of species, has an important influence on copper and cadmium plating properties, and is important in solution make-up and disposal procedures. The method presented here is very specific for a given metal and gives a distribution of the complexes of that metal since the anionic cyanide complexes are retained on the mobile phase column and the cationic aqua-complexes are not retained. This fast and precise method for cyanide analysis requires no sample preparation beyond dilution.

Typically, iron and copper as aqua-complexes are determined by titration, oxidation, and retitration which has much error since the difference of two large numbers is taken (60). Another classic method for the determination of metal cyanides is to isolate a certain metal cyanide and then to determine the cyanide content of this complex after refluxing with reagent and applying uv-visible detection (60). The metal can be determined by normal atomic absorption methods.

Ion chromatography provides an excellent means for anion analysis by using a carbonate eluent, anion separator column and a fiber suppressor column (7, 61-64). Among the applications of this technique are

the analysis of acid solutions used in metal finishing
operations, including chromium plating solutions
(typically 250 g/l chromate, 2.5 g/l sulfate) polishing
solutions (typically 721 g/l phosphate, 882 g/l
sulfate), anodizing solutions (typically 180 g/l
sulfate) and hardcoating solutions (typically 140 g/l
sulfate, 18.0 g/l oxalate). Analysis of these
solutions as wastes at the water treatment plant is
another application of this technique. Ion
chromatographic methods have been presented for the
analysis of many of these solutions (7, 61-64), but it
will be shown here that by using an AG4 column, the
peak height and area are dependent upon the overall
composition of the solution, especially the amount of
strong acid or base present. Because the acidity of
these solutions can vary widely even at analytical
concentrations over the period from initial makeup
through treatment and disposal, significant error can
be introduced unless the composition of the samples and
standards are similar. The compounds used to prepare
the standards are an important consideration. It will
also be shown that the peak heights and areas for
chromium plating and acid treatment solutions can vary
even more on an old AG4 column than when the column was
new.

Ion chromatography is also used here for analysis of organic acids by ion exclusion chromatography and suppressed conductivity detection.

Online and automated procedures are also illustrated for the analysis of metal finishing solutions by ion chromatography.

PART 2

THEORY AND BACKGROUND

2.1 Column Theory

Chromatography basically involves separation due to differences in the equilibrium distribution of sample components between two different phases. One of these phases is a moving or mobile phase and the other is a stationary phase. The sample components migrate through the chromatographic system only when they are in the mobile phase. The velocity of migration of a component is a function of the equilibrium distribution. The components having distributions favoring the stationary phase migrate slower than those having distributions favoring the mobile phase. Separation then results from different velocities of migration as a consequence of these differences in

equilibrium distributions. Chromatographic theory is well understood and illustrated (6-12). Future discussion will be limited to liquid chromatography.

Retention is necessary for separation of a component X. The thermodynamic distribution coefficient (Kx) measures the degree of retention for compound X where the equilibrium distribution between the stationary and mobile phases are (6):

$$Xm \longleftrightarrow Xs \qquad (1)$$

and the thermodynamic distribution coefficient is:

$$Kx = (X)s/(X)m \qquad (2)$$

The capacity factor k' is directly proportional to Kx and is also a thermodynamic quantity, but the capacity factor k' is a more practical quantity since it can be determined directly from the chromatograph and is given by:

$$k' = (V'-V)/V \qquad (3)$$

where V' is the retention volume of the retained component measured at the peak maximium and V is the void volume required for a non-retained peak. If equation 3 is rearranged and solved for the retention volume V', then:

$$V' = V(k'+1) \qquad (4)$$

If the flow rate (ml/min) is F and the retention time is RT', they relate to V' by:

$$V' = F(RT') \tag{5}$$

It follows that:

$$k' = (RT'-RT)/RT \tag{6}$$

Similarly, the retention time of a non-retained component is RT and is related to V by:

$$V = F(RT) \tag{7}$$

Substituting equations 5 and 7 into equation 4 gives:

$$RT' = RT(k'+1) \tag{8}$$

Equations 4 and 8 give V' and RT' which are fundamental parameters for any chromatographic process for relating volumes and times to other quantities.

The goal in any separation process is to obtain resolution which is the ability to separate one component from another. Resolution (R) is usually defined as the distance between the peak centers of the two peaks divided by the average base width of the peaks, or:

$$R = (RT''-RT')/(.5)(W''+W') \tag{9}$$

where W is the peak width determined by extrapolation of the tangents of the peak to the baseline. It is assumed that peaks are symmetrical. This is a means of measuring the degree of separation of 2 components. Resolution is also related to the 3 fundamental parameters in a chromatographic separation, if equal band widths are assumed for closely spaced peaks, by

the following:

$$R = (.25) (a-1/a) (X) (k'/1+k') \qquad (10)$$

where X is the square root of N and a is the separation factor or selectivity defined as:

$$a = (V''-V/V'-V) = (k'''/k'') = (K''/K'); \qquad (11)$$

and N is the number of theoretical plates or efficiency:

$$N = (16) (Y) = (5.5) (Z); \qquad (12)$$

Y is the square of RT/W, Z is the square of RT/Wh, k' is the capacity factor from equation 6, and (Wh) is the peak width at half height. The use of (Wh) in equation 12 is most useful for peaks that are not completely resolved or have slight tailing. Another very useful quantity that is extensively used in this report for unsymmetrical peaks is the half width of the peak base, designated base half width (HW). The base half width is not truly half the base but instead is the portion of the base to the left or right of the apex perpendicular. By using HW, only the closest halfs of two peaks are used to calculate resolution. For this calculation, adding the two HW's of a peak gives its width (W). For these reasons, HW is more useful than W or Wh. For this report, RW and LW represent the right and left respective half base widths.

The thermodynamic quantity a is governed by the

relative solute distributions between the 2 phases and can be predicted by hydrogen bonding, acid-base relationships, etc. Modification of the phases changes a (6). For any two chromatographic peaks, the k' of the latter eluting peak is used in resolution equation 10.

The capacity factor k' is related to the retention of a component in terms of column volume. After the retention volume of the non-retained peak is found, it is divided into the retention volume for a retained peak to get the capacity factor for that component. The larger k', the longer a peak will be retained. Optimization of a many component sample requires that the k' values of the bands are between 1 and 10 to maximize resolution and minimize retention.

For the sample capacity, the linear distribution coeffecient with respect to sample concentration is a linear sorption isotherm. Nonlinear isotherms result from large sample sizes commonly used in LC, especially in adsorption systems. Stationary phase sample capacity is the amount of sample that is sorbed before overloading occurs. Overloading gives unsymmetrical peak shapes, retention time changes, and resolution loss (6).

Resolution can be improved by increasing k', N,

and a. Increasing a has the greatest effect on increasing resolution because the peak widths narrow. Lastly, increasing k' only slightly improves resolution since the peaks broaden. Baseline resolution usually occurs when R values are greater than 1.5.

If N is constant, then W is directly proportional to T. For a symmetric peak:

$$A = H \, W \, / \, 2 \tag{13}$$

where H and W are peak height and baseline width. If there is baseline resolution, constant area, and constant N, then H is inversely proportional to RT. If peak heights are analyzed then k' must be constant but quantitative determinations can be done in slightly non-linear isotherm regions (14).

Selectivity (a) is the net retention time ratio for two components and is equal to the ratio of the equilibrium distribution coefficients. When a= 1 then R= 0 and peaks are not resolved. The greater a is above one, the more selectivity increases, and the easier the separation will be. Large resolution changes occur with small changes in a. High a values may give excellent separation on low efficiency columns.

The number of theoretical plates (N), from equation 12, is a measure of band dispersion for the

chromatographic system. The smaller the band dispersion, the higher the value of N. Efficiency is a measure of how well or poorly the column was packed. The size, size distribution, and porosity of the particles also affect the value of N for the column. Smaller particles give greater efficiencies of separation because they shorten diffusion paths and minimize band dispersion. Also, the better the uniformity or the particle size and packing, the greater the efficiency of the column. Non-uniform particle size broadens bands since sample components travel at different speeds through void space and resin particles. With uniformly packed and sized particles, the diffusion paths are the same in all directions, identical components travel at the same speed, and band broadening is minimized. Another thing that contributes to band dispersion is longitudinal diffusion of the sample in the mobile phase and the kinetics of mass transfer between the stationary and mobile phase. These kinetics may be the main cause of band spreading and determine the column's efficiency. The kinetics of mass tranfer is the rate of movement of sample molecules between the mobile and stationary phases.

Each ion should ideally be continually transferred

in and out of the stationary phase on the column.
When this ion is in the stationary phase, it is
retained and falls behind the center of tne sample band
as the band center continues down the column. When
this ion is in the mobile phase, it moves with the
mobile phase. This ion's velocity is faster than the
band center since the flow velocity is faster than the
band velocity. This random movement between phases
causes dispersion in the peak as some ions will be
faster and some ions will be slower than the average.
Since the mobile phase flows, the amount of solute in
this phase is not always in equilibrium with the
adjacent stationary phase. Peak dispersion is
minimized by minimizing non-equilibrium conditions and
maximizing exchange rates. Raising column temperature
also will help this.

The number of theoretical plates is a function of
column length where longer columns of the same material
have more plates. The measure of column efficiency
that is independent of column length is the height
equivalent to a theoretical plate (HETP); this is
useful for comparing columns of different lengths. The
required equation is:

$$HETP = L/N \qquad\qquad\qquad (14)$$

where L (mm) is the column length and N is the number

of theoretical plates. The smaller HETP, the higher
the column efficiency. Efficiency measures the ability
of the column to minimize the band spreading and is
affected by: linear velocity (U), particle size (dp),
column length (L), sample amount and sample size.
Lower linear velocity increases N, except at very low
velocities. Smaller particle size increases N. Higher
temperatures reduce viscosity and increase N.
Increasing the sample amount and size decreases N. The
band dispersion term for N is a square root function as
shown in equation 10 for resolution, and doubling N
requires increasing the efficiency fourfold.

For example, an increase in the flow rate gives an
increase in effective HETP due mainly to mass transfer
broadening for the chromate case (14). For flow rates
between 1-3 ml/min the HETP varies less than 20%, with
HETP varying from .1-.2 mm typically (suppressor
included) for the H vs. U plots of common anions (14,
65). The relation of k' to the eluent molarity for
chromate, is in general, nonlinear and related to
sorption isotherm character. The eluents used here are
shown to be ideal (14).

Variation of the distribution ratio Dc causes
curvature in plots of C' (total concentration of all
forms of solute in this phase) versus C'' (total

concentration of all forms of solute in this phase).
These are partition isotherm plots, even though they
represent Dc and not Kp. The ideal situation has a
linear relationship where Dc remains constant. If the
curve levels off as the concentration approaches
mono-layer coverage of the adsorbent, then this is an
isotherm frequently encountered when C' is an adsorbed
phase (11).

Adsorption is a distribution or partitioning
process at an interface or surface. Types of
partitioning are bulk phase adsorption and interfacial
desorption. Langmuir behavior results from hydrogen
bonding, for example, and arises when a small amount of
adsorbent uses up the most active sites so that
additional adsorption is decreased. This results in
tailed peaks. At low concentrations the isotherms are
linear (8).

Non-linear isotherms exert a major influence on
peak shapes. The Langmuir adsorption isotherm tends to
bend over at high mobile phase concentrations Cm and
the resulting peak shows a substantial tail behind the
maximium concentration while the leading edge of the
peak is very abrupt. As the total quantity of solute
increases, the fraction in the mobile phase increases
and the areas of highest concentration migrate with

the greatest velocity. The fast moving high concentration center catches up with the relatively slow moving front and moves far ahead of the relatively slow moving tail and the gaussian peak is changed (11).

Tailing is cause by two processes. One is the normal partitioning or adsorption of sample and is sought for separation and has good sorption-desorption kinetics at the given velocity. The second is adsorption of solute molecules at a few particularly active sites which have very bad sorption-desorption kinetics. Once a molecule is adsorbed at such a site, it is released only after the peak is well past. There are not many of these sites but the effect is quite noticeable. The tailing appears to decrease at high sample loads because the active sites become saturated, and the percentage of solute molecules affected becomes smaller as does the relative tail size. Tailing caused by active sites can be minimized by adding a highly polar compound to the eluent to preferentially adsorb at the active sites (11).

Another factor that leads to tailing and zone broadening is sample overloading of the stationary phase; this effect can be minimized by reducing the sample size.

In most real systems, K is not constant and is

dependent on solute concentration in the stationary and mobile phases, the partition isotherm is usually non-linear and the ratio C_s/C_m is not constant. Particularly in adsorption chromatography, the adsorption isotherm tends to bend over at high C_m values as a result of crowding of adsorbed species on the adsorbent surface although if small amounts of material are used then problems are minimial. Equilibration may not be rapid compared to the movement of the mobile phase. Diffusion and re-distribution are never instantaneous and material may be swept along in the mobile phase before it equilibrates, which lowers efficiency (N). Longitudinal diffusion is of particular importance at low flow rates where substantial time is present for mobile phase material to broaden the chromatographic zone.

There are three theories that describe the contributing factors which lead to band broadening and calculation of HETP. Given in order of increasing complexity, they are plate, rate and generalized non-equilibrium theories (11).

Plate theory incorrectly assumes a linear isotherm and ideal diffusion situation (linear-ideal). It does not consider the flow rate a variable and does not consider the distances over which diffusion occurs.

Rate theory does consider the physical processes occuring during zone migration (11).

Rate theory considers equilibrium rates, rates of diffusion in both phases and is of a kinetic type (linear-nonideal). Van Deemter developed rate theory and the van Deemter equation plots plate height as a function of mobile phase velocity. In this approach, the overall HETP is considered to be made up from several components:

$$HETP= HETPdm + HETPds + HETPem + \qquad (15)$$
$$HETPes + HETPf$$

where:

HETPdm represents mobile phase diffusion

HETPds represents stationary phase diffusion

HETPem represents mobile phase slow equilibrium

HETPes represents stationary phase slow
equilibrium

HETPf represents non-uniform flow patterns

Diffusion, slow equilibrium and non-uniform flow patterns contribute additively to the total zone broadening in terms of the variance (V) of these quantities:

$$V(total)= Vd + Ve + Vf \qquad (16)$$
$$HETP= V(total)/L \qquad (17)$$

where L is again column length.

Longitudinal diffusion causes zone broadening at low flow rates since the material spends more time in the column's mobile phase (11).

The tranfer of solute molecules between the mobile and stationary phases is not instantaneous due to slow equilibrium as a result of 2 factors. First, there is kinetic control of the rate at which molecules can cross the interface, called sorption-desorption kinetics. Second, there is kinetic control of the rate at which molecules can arrive at the interface for transfer. The second effect is due to the finite rate of diffusion of solute molecules in the phases and is called diffusion-controlled-kinetics. These 2 factors cause the chromatographic zone in the stationary phase to lag behind that of the mobile phase giving zone broadening. The zone variance varies due to slow equilibrium. It varies directly with mobile phase velocity, directly with the square of phase thickness, and inversely with the diffusion coefficient (11). Kinetic controlled zone broadening may be minimized by reducing the linear velocity (U) but not too low a value or else longitudial diffusion will increase zone broadening (11).

Rate theory is in error in assuming a linear partition isotherm for adsorption chromatography

although it is attainable for partition chromatography.

Generalized non-equilibrium theory was developed by Giddings and rigorously shows factors leading to band broadening and of the three theories, is the most useful for developing better columns (11). The approach of Giddings and his co-workers shows a column or system in dynamic non-equilibrium, where mass tranfer of the solute into the stationary phase results in a lag behind the equilibrium concentration (band center). As a result, Giddings' approach describes the column situation more accurately than the other two theories. When a solute desorbes or tranfers into the mobile phase, then it moves more rapidly than the band center. Dispersion increases with the number of tranfers and decreases as the velocity of the mobile phase decreases.

Giddings' individual band-broadening contributions to HETP can be described by a modified van Deemter equation:

$$HETP= 1/(1/HETPed + 1/HETPmp) + HETPld +$$
$$HETPsm + HETPsp \qquad (18)$$

where:

HETPsp= Solute stationary phase mass tranfer.

HETPsm= Solute stagnant mobile phase mass tranfer; in pores mass tranfer increases (diffusion

is increased) by decreasing pore depth or particle size, decreasing mobile phase velocity, decreasing stationary phase thickness, and lowering the solute k'.

HETPmp= Solute mobile phase mass tranfer is due to flow patterns and is minimized by uniform packings, particle sizes, inter-particle channels and low viscosity.

HETPed= Eddy diffusion due to differing flow paths and non-uniform packings.

HETPld= Longitudinal diffusion which is random diffusion in and against the direction of mobile phase flow and is low in LC (high in GC) except at very low LC flow rates.

These quantities can be defined alternately as:

HETPed= Ze dp		(19)
HETPmp= Zm dp dp U / Dm		(20)
HETPld= Zd Dm / U		(21)
HETPsm= Zsm dp dp U / Dm		(22)
HETPsp= Zs dp dp U / Ds		(23)

where:

dp= Particle diameter.

Dm= Solute mobile phase diffusion coefficient.

Ds= Solute stationary phase diffusion coefficient.

U = Mobile phase linear velocity.

Ze, Zm, Zd, Zsm, Zs are Giddings' coefficients for the quantities above.

HETPed, HETPmp, HETPsm and HETPsp are small with low flow rates while HETPld is small with high flow rates. High U gives low R and N.

HETP versus U curves are determined experimentally and the optimium point of operation for analysis has velocity (proportional to chromatographic flow rate) just above the HETP vs. U minimium on the high velocity side of this minimium (11). Low HETP results from low dp, U, viscosity, and uniform packings.

A plot of HETP (y-axis) versus U (the linear velocity: x-axis) shows that HETP increases at low flow rates due to longitudinal diffusion but also increases at high flow rates due to slow equilibrium and flow patterns. Flow pattern zone broadening is due to the many different length paths the mobile phase has available to follow (11).

Pellicular packing has improved HETPsm, HETPsp, and N but give low Vs and sample capacity compared to traditional packings (6).

Zone broadening outside the column may come from the feed volume, mixing chamber, detector volume, etc (11).

In absorption chromatography, the most important

characteristic of an adsorbent is its activity, the extent it will retain solute species. Activity is a function of strength and density of active sites on the adsorbent surface, surface area, and water content of the adsorbent material. The apparent activity depends on the mobile phase and the solutes; and the affect they have on the adsorbent. These adsorbents have polar active groups. Water molecules will mask these sites to some extent. Hydrogen bonding is the primary adsorption interaction between the active sites and the polar solutes, differing from ion exchange chromatography (11).

The mobile phase competes with the solute for adsorption sites. Changing the mobile phase will affect the degree the solute is adsorbed and this is usually in a non-linear fashion. Tables called elutropic series give eluent strength parameters which are proportional to the eluent adsorption energy per unit area (11).

Ion exchange and thus ion chromatography depends on the separation of ionic species, and may involve solutes that are only partially dissociated.

The ionization of weak acids has the following equilibrium and equilibrium constant (10):

$$HA \longleftrightarrow H^+ + A^- \tag{24}$$

$$K = (H^+)(A^-) / (HA) \quad (25)$$

The pH of a strong acid such as .01 N HCl equals:

$$pH = -\log(H^+) = -\log(.01) = 2 \quad (26)$$

since the acid is totally dissociated.

For a weak diprotic acid, the equilibria and equilibrium constants are (10):

$$H_2A \longleftrightarrow H^+ + HA^- \quad (27)$$

$$HA^- \longleftrightarrow H^+ + A^{2-} \quad (28)$$

$$K' = (H^+)(HA^-) / (H_2A) \quad (29)$$

$$K'' = (H^+)(A^{2-}) / (HA^-) \quad (30)$$

If K' is much larger than K'', then the pH is determined by the value of K':

$$K' = 10^{-2.85} = (H^+)(HA^-) / (H_2A) \quad (31)$$

$$K' = 10^{-2.85} = (H^+)^2 / .15 - (H^+) \quad (32)$$

The hydrogen ion concentration is .0138 M and the pH is 1.86 for the weak acid.

The equilibrium constants can be used to calculate the ratio of dissociated acids at a given pH. The acetate ion/ acetic acid ratio at pH=5 is (10):

$$Ka = (H^+)(Ac^-) / (HAc) = 1.8 \times 10^{-5} \quad (33)$$

$$1.8 \times 10^{-5} = (10^{-5})(Ac^-) / (HAc) \quad (34)$$

$$1.8 = (Ac^-) / (HAc) \quad (35)$$

Salts of carbonic acid, boric acid and phenol make good eluents for suppressed ion chromatography (IC) in which electrolytic conductivity is used for

detection, because acids formed in the suppressor are only slightly ionized, with pKa's from 7 to 11 as seen in Table 1 (12). The suppressor forms weakly ionized species or water from the eluent. Anion acids analyzed by suppressed IC should have pKa's less than seven. Cyanide, borate, and phenoxide are difficult to analyze by suppressed IC since pKa is about 10 as seen in Table 1.

Strong acids have pka's from 0-2 with IC the method of choice and weak acids are from 2-7 with ion exclusion chromatography (ICE) the prefered method (61). ICE uses Donnan exclusion to acheive component separation. These approaches are described in more detail in section 2.3.

Ideally the eluent anion exhibits a marginally higher affinity for the resin than does the strongest retained sample ion but this needs to be optimized to consider the weakest retained anions. An intermediate strength eluent may be necessary to accomplish separation of all components. Table 2 is a list of common anion eluents (12):

NaOH can be added to carbonate eluents to change eluent pH. At high pH, phosphate elutes after sulfate and at low pH, biphosphate is before sulfate (12). The negative two charge of carbonate gives good

Table 1. Ionization Constants of Acids (12)

Acid		pKa at zero ionic strength
acetic		4.76
benzoic		4.20
boric		9.23
carbonic	pKa	6.37
	pKa'	10.32
citric	pKa	3.13
	pKa'	4.77
	pKa''	6.40
chromic	pKa	-0.98
	pKa'	6.50
EDTA	pKa	1.99
	pKa'	2.67
	pKa''	6.16
	pKa'''	10.26
formic		3.77
hydrochloric		-1.00
hydrocyanic		9.31
hydrofluoric		3.17
nitrous		3.29
oxalic	pKa	1.06
	pKa'	9.29
phenol		9.85

Table 1. (Con't) Ionization Constants of Acids (12)

Acid		pKa at zero ionic strength
phosphoric	pKa	2.12
	pKa'	7.21
	pKa''	12.32
o-phthalic	pKa	2.92
	pKa'	6.41
sulfuric	pKa	-1.00
	pKa'	1.92
tartaric	pKa	3.04
	pKa'	4.37

Table 2. Common Anion Eluents

Eluent	Eluting Ion	Strength	Suppressor Reaction Product
sodium borate	borate	very weak	boric acid
sodium hydroxide	hydroxide	weak	water
sodium bi-carbonate	bicarbonate	weak	carbonic acid
sodium carbonate	carbonate	medium	carbonic acid

eluting characteristics. Variation of the sodium
bicarbonate/ sodium carbonate ratio in turn varies
selectivities, eluent pH, and run time (12).
Electrostatic differences and ionic size/ charge
effects make carbonate a stronger eluent than
bicarbonate and make bicarbonate a stronger eluent
than hydroxide (14,46).

The carbonate/ bicarbonate/ hydroxide
concentrations in standard carbonate eluent are given
by the following (30):

$$\log h = \text{hydroxide} = pH - 11.0 \tag{36}$$

$$\log (c/b) = pH - 10.33 \tag{37}$$

$$b = \text{bicarbonate} = (t-h)(1+2(c/b)) \tag{38}$$

$$c = \text{carbonate} = b(c/b) \tag{39}$$

$t =$ Total alkalinity by titration.

The retention order for some common ions are:
hydrogen ion < sodium ion < hydroxide ion < bicarbonate
ion < chloride ion < sulfate ion and < chromate ion;
this is due in part to ionic size effect due to steric
stress buildup in the resin. For chloride, nitrate,
sulfate, carbonate, and bicarbonate ions, the
respective ionic sizes in Angstroms are 1.81, 1.89,
2.30, 1.85, and 1.63.

As mentioned above, high performance ion
chromatography (HPIC) is useful for acidic species with

pka's less than 7, and can be used for a pH range of 0-14, with wide selectivity. Also resins are available with low capacity/ high efficiency, capable of high flow rates and chemical suppression (61).

2.2 Chromatographic Instrumentation

A typical chromatograph consists of a delivery portion containing the eluent reservoir, pump, and sample injector; the separation portion containing the separator column; the detection portion containing the suppressor column and the detector; and the data handling portion which may contain an integrator and/or computer. Two major types of pumps are used to provide a constant and precise eluent flow; constant pressure (Dionex) and constant displacement. A typical injector is the loop valve type (Dionex) for injection volumes greater than 10ul into the eluent flowstream. For ion chromatography, 3 types of separator columns are used: high performance ion chromatography (HPIC), high performance ion chromatography exclusion (HPICE), and mobile phase ion chromatography (MPIC) and these columns are the most important part of the system. The details of these different modes of separation are

described later.

Isocratic elution has constant eluent composition while gradient elution uses a changing composition and requires regeneration. Eluent strength is determined by trial and error. High eluent strength has a low k' and low strength has a high k' (6). Only isocratic elution was used for the work of this report.

The detector measures the amounts of components in the column effluent and should have high sensitivity, low noise, a wide linear range, wide ionic response, low sensitivity to flow and low sensitivity to temperature fluctuations. Generally, there are five types of detectors used: they are the conductivity, electrochemical, UV-visible, refractive index and fluorescence types. If low conductivity eluents are not used, then a suppressor column is required before the conductivity detector in order to chemically convert the high conductivity eluent to a low conductivity form before detection. Also, post column reaction may be necessary before detection.

The data handling portion of the system gives the retention times for the peaks and identifies a specific component. For each peak, the peak height or area is used to quantify that component against standards.

The particular ion chromatograph used in this work

is the Dionex model 2020i system.

2.3 Modes of Separation

The ion chromatograph (Dionex) easily performs sub-ppm analysis of most ions. Typically, polystyrene/ divinylbenzene resins are used in the columns. High Performance Ion Chromatography (HPIC) columns have capacities of .01-.05 meq/g, High Performance Ion Chromatography Exclusion (HPICE) columns have 3-4 meq/g and Mobile Phase Ion Chromatography (MPIC) columns have a variable ion exchange capacity. MPIC ion exchange capacity is related to the eluent and there are no ion exchange sites on the resin.

HPIC is used for common inorganic ions such as fluoride, chloride, nitrate, sulfate, sodium, potassium, Mg(II), Ca(II), Fe(III), Zn(II), Ni(II), etc., polyvalent anions, and carbohydrate analysis; MPIC is employed for hydrophobic ions such as alkyl and aryl sulfonates and sulfates, quaternary amines as well as iodide, thiocyanide, chlorate, and fluoroborate; HPICE is useful for organic and amino acids and group separation of organics and inorganics. Using coupled HPIC/ HPICE, very complex samples such as urine, plasma, and food may be analyzed. To acheive

separation, MPIC uses ion pairing, HPIC uses low capacity ion exchange, and HPICE uses high capacity ion exchange dominated by Donnan exclusion.

The 5 major variables of IC resins are: material, crosslinking, particle size, functional groups, and capacity. In the polystyrene/ divinylbenzene copolymer, the divinylbenzene forms the crosslinks between the styrene molecules. Greater crosslinking results in less resin swelling, slower diffusion of ions with large hydrated radii, smaller void volumn, less HPICE separation, lower system pressure for a given flow rate, more rigidity, and lastly less susceptibility to osmotic shock and particle breakage due to swelling and contraction when changing the mobile phase.

Smaller resin particles lead to the requirement of higher system pressure for a given flow rate, but also to the greater efficiency of separation because the smaller particles shorten diffusion paths and minimize band dispersion.

Sulfonic acid and quaternary amine type funtional group resins are used. Porous resins have funtional groups throughout the beads (HPICE) while pellicular resins have only surface groups on the beads (HPIC).

The capacity of an ion exchange resin is defined

as the number of funtional groups in a unit volume or mass of resin. Ion exchange capacity is expressed in milliequivalents per gram (meq/g) and the higher it is, the stronger the eluents necessary for time efficient separation; 1-10 meq/g is typical.

HPIC cation resin has an inert hydrophobic core with surface sulfonic acid groups which are covalently bound to the copolymer. Moderately low capacities with high efficiencies are acheived by limiting functional groups to the surface so that diffusion path distances to exchange sites are shorter.

The anion separator resins are similar to the cation separator resins and also have a hydrophobic core with sulfonic groups attached to the bead surface. To these sulfonic groups are attached very small totally porous anion exchange beads which are aminated beads that are strongly held by coulombic forces that can withstand 5 M sodium hydroxide eluent. Van der Waals forces from the copolymer and the beads also contribute to holding the beads in place. Due to geometry, not all the sulfonic acid sites are occupied with aminated particles. This leaves exposed sites that can bind cations, such as Ca(II) or Mg(II), and may cause significant problems; such as when determining low level phosphate. The separation

mechanism is due to exchange of anions between the mobile phase and the cationic sites. Eluent anions and sample anions compete for cationic resin sites. Because ions have different exchange site affinities, mixtures can be separated. Anion exchange is summarized by:

Solute + Eluent-Aminated Resin <-->

Solute-Aminated Resin + Eluent   (40)

and cation exchange is summarized by:

Solute + Eluent-Sulfonated Resin <-->

Solute-Sulfonated Resin + Eluent   (41)
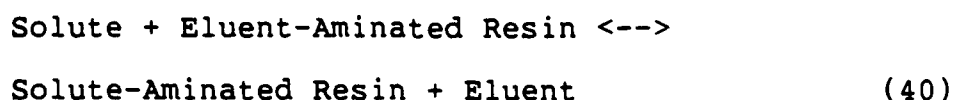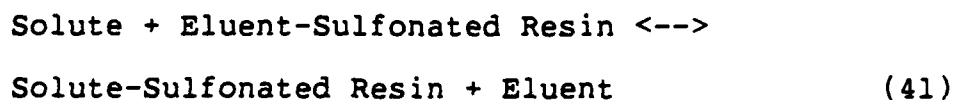
Each equation has an equilibrium constant which is the distribution coefficient K as described earlier. The distribution coefficient is a function of ionic charge, ionic size, ionic eluent strength, pH, and resin type. The more strongly the ionic solute interacts with the ion exchange resin, the longer its retention time. The greater the sample's ionic charge, or the greater its polarizability, the greater the resin affinity and the greater the elution time. The greater resin affinity, the stronger an eluent must be to give a reasonable elution time. For ions of the same valence, the larger the hydrated ionic size, the more polarizable the ion, the stronger it is attracted to the resin, with consequently longer elution time.

Eluent pH affects the equilibrium distribution of multivalent or multifunctional ions since resin affinity is related to charge. Bronstead acid-base equilibrium which is governed by the pH of the mobile phase will determine the charge of the predominant species present (e.g., for a weak diprotic acid, the neutral acid will predominate at a low pH, the monoprotic species will predominate at an intermediate pH, while the unprotanated species will predominate at a high pH).

Resin selectivity substantially affects separation by affecting equilibrium distribution of the sample and eluent. Selectivity is a function of crosslinking, bead sizes and functional groups.

The Dionex AG4 anion separator column, a popular column of established design, has 3% crosslinking, aminated type functional groups, 200-4000 Angstrom size beads, 15 micron substrate size, 10000 plates/ meter efficiency, 700-900 psi operating pressure, and 4x250 mm dimensions. Typical HETP values are in the range of 0.1 mm. Eluent strength increases from hydroxide, bisulfate, carbonate to iodide eluent ions. Information on the new CG2 cation/ transition metal separator columns is proprietary.

Separator column life depends on the sample

matrix. Pressure is not a variable in practical IC or LC. HPIC guard columns are smaller analytical columns which are also used to trap particulates. These columns are used alone for highly retained ions.

HPICE uses closely-sized, totally sulfonated ion exchange resins of controlled crosslinking. Donnan exclusion is used and limits the ability of anions to move across a semi-permeable membrane area into the pore volume of the resin. Non-ionized species are permitted to permeate into the pores of the resin and acheive retention. The semi-permeable membrane is formed by the functional groups of the resin and exists between the interstitial eluent liquid of the resin particles and the occluded liquid inside the resin pores. Retention is a function of total pore volume and resin surface area. HPICE is similar to steric exclusion chromatography where separation is based on the ability of the solute to enter pores of the resin, migrate back into the eluent, and species size and shape are important. HPICE is also dependent on pore diffusion but retention can be controlled by the degree of species ionization which is pH dependent; pH and ionic strength affect the distribution coefficient. The higher the pH, the greater the ionization, and the less the retention by ion exclusion. The larger the

solute pKa, the longer the retention time. Increasing the temperature will increase ionization and decrease retention. Concentration is important for weak electrolytes since ionization is a function of concentration. The lower the eluent pH, the longer the retention of weak electrolytes. The higher the crosslinking, the lower the volume and the less the resulting separation. The polymer type, the relative hydrophobicities, and the functional groups affect retention. Van der Waals forces affect the elution of alphatic and aromatic species. Since separation is diffusion dependent, slow flow rates are needed, about 1 ml/min.

For HPICE resins, aromatic ions are sorbed by ionic forces and like-like attractions. Non-ionic species are also separated by a partition mechanism. Buffers decrease mobile phase solubility and increase resin affinity. Resin affinity decreases as the radius of the hydrated ion increases (6).

HPICE may be coupled to HPIC so that strong and weak acids/ salts may be separated and analyzed interference-free or may be concentrated on a column for later analysis. Also, organic and inorganic acids may be separated and analyzed.

HPICE uses an acidic eluent (HCl) to suppress weak

acid ionization with suppressed conductivity detection.
The chemical suppression of HCl is by an Ag(I) form
resin:

HCl + (resin-Ag) -->

AgCl(s) + (resin-H)   (42)

There is no information available on the HPICE-AS1
separator column for organic acids since it is
proprietary.

MPIC uses a resin with no fixed ion exchange sites
with an eluent containing an ion pair reagent and an
organic modifier. Component separation is very similar
to ion-pair chromatography. The column consists of a
polystyrene/ divinylbenzene copolymer resin and uses
suppressed conductivity detection to give high
efficiency and selectivity for hydrophobic ions. The
technique is not as good for hydrophillic ions since
adsorption type separation is less dominant. MPIC can
be effectively used for ions that exhibit extremely low
or high affinities for other ion exchange resins. The
mechanism of MPIC involves an electrical double layer
model with both adsorption and dynamic ion exchange. A
hydrophobic ion penetrates the inner electrical double
layer Helmholtz region where retention is dominated by
adsorption. Hydrophillic ions penetrate only the outer
electrical double layer Helmholtz region where

retention is dominated by ion exchange. Organic modifiers such as acetonitrile can be used to control retention for adsorption cases with no effect from varying ionic strength. Variation of ionic strength or organic modifiers can be used to vary retention in the outer Helmholtz region. The mobile phase, stationary phase, and ion pair reagent all influence MPIC. As the ion pair approaches the neutral MPIC resin surface, adsorption occurs and the degree of interaction depends on ion pair hydrophobicity. The more hydrophobic, the more interaction and the more retention of the ion pair. For MPIC cation separations, an aliphatic sulfonic acid is used as the ion pair reagent with acetonitrile as an organic modifier. For MPIC anion separation, a quaternary ammonium hydroxide is used as the ion pair reagent. The more hydrophobic the analyte ion, the smaller the ion pair reagent chain necessary.

MPIC resin has high crosslinking, very large surface area for adsorption effects, and does not swell with organic solvents. Nine factors control retention and selectivity in MPIC. First, the more hydrophobic the pairing ion, the greater the resulting retention. Second, an increase in pairing ion concentration will increase retention to a limit, after which it decreases. Third, retention decreases with increasing

organic modifier concentration. Fourth, retention increases with a more hydrophobic stationary phase. Fifth, pH changes cause solute ionization and greater retention. Sixth, retention decreases as the temperature increases with increased efficiency and decreased selectivity. Seventh, increased ionic strength decreases retention by affecting ion pairing. Eighth, retention will decrease as the organic modifier is more non-polar. Last, increased counter ion concentration decreases retention by affecting ion pairing.

2.4 Modes of Detection

The detection modes commonly used in ion chromatography are: suppressed and unsuppressed conductivity; amperometry; pulsed amperometry; uv-visible spectroscopy; and fluorescence.

Conductivity detection depends on the change in electrolytic conductivity caused by the eluded sample; it has a wide linear range, high sensitivity, and is useful for ions with pKa's less than seven.

Amperometric detection depends on the current that flows when an oxidizable or reducible substance is involved, and is used for ions such as cyanide,

sulfide, bromide, iodide, hypochloride, etc. at ug/l
levels. Pulsed amperometry uses many different applied
potentials to detect carbohydrates, alcohols, phenols,
cyanide, sulfide, bromide, iodide, hypochloride, etc.

UV-visible detection uses optical absorption
methods to detect absorbing species. A reagent may be
added after the column using a post column reaction to
enhance absorbance of weakly absorbing species like
transition metals. Also, sulfide, nitrate, bromide,
iodide, aromatics, and organic acids may be detected in
this way. Fluorescence detection with HPICE is used
for aromatics and amino acids with a post column
reagent necessary.

Conductivity is the most widely used method of
detection for ion chromatography and is based on
electrical conductivity of an ionic solution which is
placed between two oppositely charged electrodes. The
presence of these ions allows electrical current to
flow between the electrodes, completing the circuit.
At low concentrations, conductivity is directly
proportional to the concentration of conductive
species. Concentration and temperature affect
conductivity linearity.

About fifty inorganic and fifty organic anions can
be determined by IC and conductivity detection (12).

Conductivity detection will not detect molecular species.

Dionex uses chemically suppressed detection. In this process, the conductivity of the eluent is lowered by ion exchange (column or fiber) before detection. The suppressor changes the highly conductive eluent ions to species that are significantly less conductive. As solute ions pass through the suppressor, they are converted to their corresponding highly conductive acids and hydroxides. Both of these changes contribute to increased detection sensitivity.

In anion exchange chromatography, where sodium carbonate eluents are used, the carbonate is converted in the suppressor column to low conductivity carbonic acid and the sodium ions are attached to the resin. For cation exchange chromatography, where hydrochloric acid eluents are used, the chloride exchanges with hydroxide ions on the resin and the protons form low conductivity water with these hydroxide ions. Also, metal chlorides are converted to more highly conductive hydroxides. Disadvantages of column chemical suppression are: the need for periodic regeneration; the Donnan exclusion effect on weak acids causing higher retention; and the Donnan exclusion effect on the water dip also causing higher retention of less

retained ions due to displacement. The water dip is caused by sample water having lower conductivity than the suppressed eluent.

The fiber suppressor was developed to eliminate all of the above disadvantages of the column suppressor, and it enhances sensitivity. It has no down-time for regeneration, no ion exclusion problems, uses a membrane instead of resin beads, and is used for both cations and anions. The regenerate continuously flows on the outside of the fiber membrane with eluent and sample on the inside. The same ions exchange as on a packed column suppressor. However, a fast eluent flow rate will not allow sodium ions in the center of the fiber regenerator to be exchanged for protons since the diffusion to the fiber wall takes more time than allowed, thus leading to decreased sensitivity (66).

HPICE chemical suppression was explained above. The organic sample acids enter the detector as free acid and some Ag(I) salts.

MPIC chemical suppression removes the ion-pair reagent from the eluent by exchanging it with hydrogen or hydroxide ions to form water for anions and cations, respectively. The solute ions are converted to their more conductive acid or hydroxide form by the same process.

Systems that use no chemical suppression are limited to low conductivity eluents for conductivity detection.

Conductivity cell current is due to both anions and cations. At higher concentrations, conductivity is limited by the degree of ion dissociation, ionic molility, and ion-pair formation. For weak acids and bases, detection is limited by the degree of dissociation. Dissociation depends on the solute and eluent. As concentration increases, the ratio of ionized to non-ionized species decreases, less current is carried, and deviations occur in detector linearity. For weakly dissociated species, the linearity range depends on pKa values.

For strong acids and bases and their salts, which are completely dissociated, ionic mobility limits detection linearity. Ionic mobility is the migration velocity of an ion in an electrical field in which the potential changes 1 volt/ cm in the field direction. It is temperature dependent; the higher the temperature, the higher the ionic mobility. High conductivity values are most sensitive to temperature, exhibiting baseline oscillation due to room temperature fluctuations. Reproducibility and linearity may also be affected. Chemical suppression slightly reduces

this effect. There is a temperature compensation select unit on conductivity detectors that can compensate for the temperature effect for most eluents (1.7 percent/ degree Celsius is commonly used). Ions with high charge density, allowing for hydration, have high mobility. At high concentrations, the importance of the interactions among the ions of strong electrolytes increases, giving lower ionic mobility.

A solution conducts current between two electrodes across which an electric potential is applied and obeys ohms law:

$$V = IR \qquad (43)$$

Conductance (G) of a solution is expressed in terms of the reciprocal of the solution resistance (R) in units of sieman (S) where (12):

$$G = 1/R \qquad (44)$$

Specific conductance (k) takes into account the area of the electrodes (A) in square centimeters and the distance (1) between electrodes in cm:

$$k = Gl/A \qquad (45)$$

and k is typically expressed in S/ cm. The cell constant (K) in reciprocal cm is defined as:

$$K = 1/A \qquad (46)$$

and thus:

$$k = GK \qquad (47)$$

Equivalent conductance (E) takes into account the concentration of the solution and is:

$$E = 1000 \, k/c \tag{48}$$

where c is concentration in equivalents per cubic cm times a thousand, and E is in (square cm)/ equivalent.

From the above equations it follows that:

$$G = E \, c/1000 \, K \tag{49}$$

Conductivity values are usually in the uS range for dilute solutions using normal cells (12).

Since k is 0.0001469 and G(measured) is 147 uS for for 0.00100 N potassium chloride, the cell constant K is 0.9993 reciprocal centimeter at 25 degrees Celsius for the *Dionex system by equation* 47. *Once K is known,* the G of any other solutions can be estimated by equation 49.

Limiting equivalent conductances of common ions are given in Table 3 below. For dilute solutions 0.00001 N to 0.001 N, the equivalent conductances are nearly equal to the limiting values. The limiting equivalent conductances (e) of the anions and cations present are summed as follows to get E:

$$E = e^- + e^+ \tag{50}$$

For potassium chloride, E is given by:

$$E = eK^+ + eCl^- \tag{51}$$

and E = 150 from Table 3. From equation 49, the

Table 3. Limiting Equivalent Ionic
Conductances (e) of Common Ions in
Aqueous Solutions at 25 Degrees C

Anions	e	Cations	e
hydroxide	198	hydrogen	350
fluoride	54	lithium	39
chloride	76	sodium	50
bromide	78	potassium	74
iodide	77	ammonium	73
nitrate	71	Mg(II)	53
bicarbonate	45	Ca(II)	60
formate	55	Ba(II)	64
acetate	41	Zn(II)	53
benzoate	32	Hg(II)	53
thiocyanide	66	Cu(II)	55
sulfate	80	Pb(II)	64
carbonate	72	Co(II)	53
oxalate	74	Fe(III)	68
chromate	85		
phosphate	69		
ferricyanide	101		
ferrocyanide	111		

units for e are (sieman)(square centimeter)/equivalent.

The G expected for .001 M potassium chloride for a

typical system with the cell constant K= 1 reciprocal

centimeter is:

$$G= 150 \times .001 / 1000 \times 1$$

$$= 0.00015 \text{ S} = 150 \text{ uS} \tag{52}$$

The calculation in equation 52 is used extensively

throughout this report.

Nonsuppressed systems have more baseline noise

than suppressed systems. Also, nonsuppressed systems

have only about one order of magnitude range while

suppressed systems have about four orders as shown

below (61). A good illustration of this is for the

determination of .001 mM sodium chloride with .001 mM

sodium bicarbonate eluent. The typical conductance

values for sodium chloride, hydrochloric acid, sodium

carbonate, and carbonic acid are 12.3 uS, 40.5 uS,

8.6 uS and 3.1 uS, for the respective 0.001 mM

solutions. The unsuppressed peak signal is the

difference between sodium chloride and sodium

bicarbonate, or 12.3 - 8.6 = 3.7 uS. The suppressed

peak signal is the difference hydrochloric and carbonic

acid, or 40.5 - 3.1 = 37.4 uS. Thus, the suppressed

case is favored by a factor of 10 in sensitivity. A

typical eluent background of 0-30 uS is normal for

suppressed IC.

Conductivity is unsuitable for ions with pKa values greater than 7 but amperometric detection can be used for some electrochemically active species. Amperometric detection is based on measurement of current changes during oxidation, reduction, or formation of complexes of sample species on the working electrode surface. A potential is applied between the working and reference electrodes. When an electroactive species with an oxidation or reduction potential equal or less than this applied potential reaches the working electrode surface, its oxidation or reduction generates a current between the working and counter electrodes. This current is proportional to the concentration of the electroactive species. The detector employs reference, working and counter electrodes. The working electrode is either silver or platinum according to the application. The silver type is used for sulfide, halides, cyanide and other ions that form precipates and complexes with silver. The potential range is about 0.00 to 0.50 volt and is pH dependent. The platinum type is used for aromatics and hypochlorite. Its potential range is about -0.20 to +1.50 volts and is also pH dependent. Conductivity and amperometric detector eluents are compatible but

amperometric eluents may need an ionizable salt to increase ionic strength. The detector has ppb sensitivity, and four orders of magnitude linearity. Response is determined by (12):

$$Q = nFN \qquad (53)$$

where Q is the charge passed in coulombs, n is the number of electrons that flowed in the reaction, F is Faraday's constant and N is the number of moles of electro-active substance oxidized or reduced.

The pulsed amperometric detector uses a gold electrode for carbohydrates, a glassy carbon electrode for aromatics, and silver and platinum electrodes for the same species as in the unpulsed methods. The pulsed method has the advantage that working electrode surfaces need much less cleaning since the current flow is pulsed. The range of the detector is from plus to minus 2.00 volts.

The uv-visible detector can be used with or without chemical suppression and has a wavelength range between 200 and 570 nm. Spectroscopic detection is based on the characteristic absorption of electromagnetic energy by certain molecules. The absorbed energy promotes outer valence electrons from a ground state to a higher energy state and the wavelength or energy involved depends on the chemical

level within the molecule and is characteristic of that molecule.

A photosensitive detector cell measures the intensity of a beam of monochromatic light as it passes through the sample cell. When molecules absorb part of the light, the detector has a decrease in beam intensity. The decrease is directly proportional to the concentration of the absorbing molecule in the sample. The detector is used for nitrates, amines, halides, aromatics, olefins, $=C=O$, $=C=S$, $-R-N-O$, $-N=N-R$ groups, and complexed transition metals.

The optical system contains a deuterium lamp, lens, filter wheel, beam splitter, cell, sample detector, and reference detector. Electronic comparison of both detector signals compensates for light intensity variations.

The major considerations for selecting a wavelength for analysis are that the species must absorb strongly, and that the eluent should ideally show no absorbance at the selected value. Eluent absorbance is checked by comparing water and the eluent. For the uv-visible detector:

$$A = -\log T = e\, b\, c \tag{54}$$

where e is the molar absorptivity or molar extinction coefficient, b is internal cell length in centimeters,

into a molecule will tend to reduce fluorescence but this trend can be reversed by electron donating groups. Sensitivity can often be improved by forming post-column derivatives of non-fluorescent species.

The fluorometer consists of a quartz halogen lamp, a monochrometer to select the excitation wavelength, the quartz sample cell, a monochrometer set at a wavelength to collect fluorescent light, and a photomultiplier detector.

Increased absorbance and fluorescence are obtained by post-column reactor columns and Dionex uses a membrane fiber reactor with reagent outside the fiber and an eluent and sample inside the fiber. Transition metals, amino acids, amines, etc. are determined this way. The post-column reactor derivatizes after the separator column and before the spectroscopic detector. These derivatizing reagents attach absorbant and fluorescent functional groups to the otherwise undetectable species.

A post-column derivatization reagent must meet four conditions. First, it must have complete, reproducible reactions in seconds to avoid band broadening. Second, it must use small, concentrated reagent volumes compared to eluent volume to minimize dilutions. Third, the unreacted reagent that enters

the eluent ideally must have no response at the detector. Fourth, the reagent must be stable. Rapid and efficient PCR mixing is essential in the small chamber. A commonly used derivatizing agent for metal ions used for uv-visible detection is para-azo-resorinol (PAR) which reacts with 34 metals including Fe(II), Fe(III), Cu(II), and Cr(III) under special conditions (12).

Separation and detection of metal ions will be influenced by complex formation and values of the formation constants will be an important consideration. Table 4 gives some formation constants for important systems in this report.

Complex formation may be illustrated by the reaction:

$$(M)^{2+} + (L)^{n-} \longleftrightarrow (ML)^{2-n} \tag{56}$$
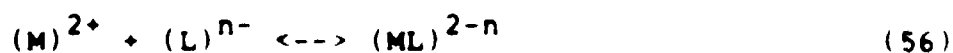
The equilibrium constant for this is:

$$K = (ML)^{2-n} / (M)^{2+} (L)^{n-} \tag{57}$$

Complexing is reduced as protons are increased:

$$(M)^{2+} + H_n L \longleftrightarrow (ML)^{2-n} + nH^+ \tag{58}$$
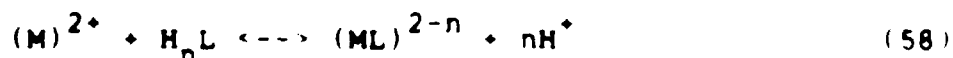
As shown, negatively charged ligands will form a lower charged or uncharged metal complex which elutes more rapidly on a cation column than the uncomplexed metal ions. Complexing species and pH of the eluent should allow only partial metal ion complexing because

Table 4. Formation Constants For Some
Metal-Ligand Complexes (10, 12)

Metal	Log K M(EDTA)	Log K M(CN)x	Log K M(PAR)
Fe(III)	25.1	-	25.0
Fe(II)	14.3	-	18.0
Cr(III)	23.0	-	27.0
Cu(I)	-	35.0	-
Cu(I)	18.8	-	21.0

too strong a complex may give no retention or separation (10, 12). Negatively charged complexes may be formed which, if stable enough, can be separated by anion chromatography.

Atomic absorption detection is not a common chromatography technique, but it is discussed here due to its applications in this report. In this method, a sample solution is aspirated into a flame and the inorganic compounds thermally dissociate into atomic vapor. The flame species absorb energy at characteristic wavelengths from a light source that emits at these wavelengths. This decreases the radiant power transmitted through the flame. Measurement of this absorption permits determinations of the sample concentrations. By using radiation with a wavelength specific for the element of interest, its detection is independent of other elements that may be present.

Most metals can be analyzed by atomic absorption detection to ppm levels. This detector consists of an element specific hollow cathode lamp radiation source, a 200-650 nm range monochrometer, a photomultiplier type detector, air-acetylene fuel, nebulizer and burner system. The end of the chromatograph flowstream outlet is connected to the inlet aspiration line of the atomic absorption spectrometer. The flow rate of the ion

chromatograph should be slightly less then the aspiration rate of the atomic absorption for ideal coupling of the two instruments. Because atomic absorption is specific for a given element, it is especially useful as an ion chromatography detector when that element is not completely separated from other components, and when that element is present in more than one chemical form.

About 60 metals and metaloids can be determined by atomic absorption methods and some non-metals such as phosphorus, sulfur and chlorine can be determined by indirect methods involving an initial precipitation of the non-metal followed by direct excess reagent analysis. No indirect methods have yet been applied using ion chromatography and indeed only a handful of direct applications have been reported as mentioned above.

2.5 Method Development

Method development is the first step for solving an ion analysis problem. Factors that affect the separation and detection of the sample are sample and matrix complexity, the required sensitivity, the speed, and the reproducibility. Optimizing a method usually

requires a compromise of packing material, eluent, and detector. Solubility, sample dilution, sample concentration and other problems contribute to sample pretreatment.

Samples should be completely in solution and free of particulates before injection or column pluging and deterioration occurs. Filtration or centrifugation are useful for dealing with this problem in complex samples.

Sample dilution may be required to bring the sample concentrations into the linear range and to lower species concentrations so column capacity is not exceeded. Column overload gives nonsymmetrical tailing peaks with low k' values. Reducing the sample loop size may help this problem. Dilution also helps minimize matrix effects which result when high concentrations of a sample species acts as an eluent and displaces the lower concentration sample species from exchange sites, giving lower k' values and poor resolution. These high concentrations may cause column overload and may be dealt with further by precipitation or neutralization techniques. High capacity ion exchange resin may also be useful for reducing matrix effects.

Sample concentration of ppb level species can be

done by on-line column concentration. This is done by using an anion separator column to replace the sample loop to concentrate the anions from sample water. The parallel method can be used for cations. Regular eluent will elute these trace sample ions.

Sample pretreatment minimizes other problems such as deterioration due to particulate or macro-molecules, column overload, and poor resolution due to matrix effects. Sample pretreatment does not help when column capacity is lowered by sample ions that have extremely high affinities for the resin. These columns may or may not be able to be treated to increase capacity and resolution. Loss of capacity is suspected when resolution gets poorer and retention times get much shorter. Guard columns can be used to protect the separator column and they are changed periodically as they are expended.

It is useful if the sample components and their approximate concentrations are known. This gives information on ion type, hydrophobic character, and pKa which helps in choosing a separator column, eluent, and detector.

2.6 Quantitative Analysis

Quantitative analysis of sample species first requires comparing retention times of the unknown peaks to that of the standards. Flow rate, temperature, and eluent strength must remain constant during this comparision. If two or more species elute at the same retention time, then the method must be modified. If the same results are obtained on the same type of column with different selectivities or by varying eluent strength, the probability of a given peak being one component increases. If many peaks are present and it is hard to identify a certain peak, then it is helpful to run the component spiked and unspiked to determine that peak.

When a component has been identified, quantitation is done by comparing detector response for the sample to that of a standard and will be precise if sample preparation errors are minimized. Solution storage problems such as volatilization, photo-reaction, air sensitivity, and adsorption or desorption of trace species on the storage container surface can cause error. Sample pretreatment problems such as dilution errors, filtering errors, co-precipitation, or adsorption also cause problems.

Separation should be optimized for analysis such as by minimizing peak overlap and tailing. Separation

of overlapping peaks is done by weakening the eluent or
lengthing the column. Tailing caused by column
overload is minimized by diluting the sample. Tailing
caused by adsorption is minimized by an organic
modifier or temperature increase.

After separation is optimized, the peak height or
area is easy to measure from the integrator as a
function of detector response. In general, peak height
measurements are more reliable than peak area
measurements as long as physical chromatographic
conditions are constant. Areas are more in error than
peak heights due to the variability of a typical
integrator in determining the beginning and the end of
a peak. Peak heights are more reliable since only the
maximium and minimium of the peak needs to be
determined. For varying chromatographic conditions,
however, peak area reproducibility is less sensitive
to error.

Peak height (H) is the distance from the baseline
to the peak maximium. Baseline drift requires that the
baseline be interpolated from start to finish. Peak
height should not be used where there is extreme drift,
column overload, or peak shoulders because in these
cases height is not linear with area. Peak height has
less than two percent precision error with correct

calibration.

Peak area (A) can be approximated by the peak height (H) times the width at half height (Wh). The Wh is used instead of base width to lower errors due to tailing and adsorption. This area method only works for standards and samples with the same peak shapes and same distortions. Peak area precision error less than ten percent is common with correct calibration. Integrators calculate areas using an approximate integration method from calculus where the area is computed from summing many discrete rectangles.

After choosing peak area or height, standards are analyzed to get a plot of detector response versus species concentration which is called a calibration curve. With this plot, a linear range can be chosen for analysis. The calibration plot has sample concentration on the x-axis and detector response on the y-axis. The ideal calibration curve intersects the origin. If the curve intersects a positive y-value at $x = 0$, then the standards were prepared with some error or there is an unresolved peak in the sample and the standard additions calibration method is used. If the curve intersects a negative y-value at $x = 0$, then the standards were prepared with some error or the columns and glassware adsorbed trace amounts of material.

The external or the standard addition methods may
be used for a calibration curve. The external standard
method is a direct comparision of peak area or height
of an unknown species with that of the same standard
species. Standards are prepared in the linear range,
and equal volumes of standards and samples are injected
for practical calibration.

The standard additions method uses a calibration
curve from which concentration of a species is
determined by back extrapolation. The sample is
measured with no standard species added, with a half
aliquot of standard species added, with one aliquot of
standard species added, and with two aliquots of
standard species added. An aliquot is chosen to
contain about the same amount of the species as the
unspiked sample. The four points are plotted and
extrapolated to the intersection of the concentration
axis. The absolute value of this number is the
concentration of that species in the unknown sample
provided uniform dilutions were used.

The standard additions method is used for samples
with matrix interferences and the major disadvantage
is the error due to working in a nonlinear calibration
range.

PART 3
EXPERIMENTAL

Several applications of ion chromatography for the analysis of solutions used in electroplating or metal finishing have been developed in this project. The following gives the common details of the experimental procedures, materials and apparatus employed.

A model 2020i Dionex ion chromatograph was used which includes a Dionex autosampler, a Dionex controller, and a Dionex 4270 integrator. Detectors used were the following: Dionex suppressed conductivity (SCD); Dionex filter uv-visible (FD), Hewlett-Packard diode array uv-visible (DAD), and Perkin-Elmer atomic absorption (AA).

All chemicals were analytical reagent grade quality. All salts were dried at 110 degrees Celsius overnight before dilution unless otherwise indicated. All solutions were prepared with 18.3 mega-ohm purity deionized water dilution. Each data point reported represents an average of six runs unless otherwise indicated. For a given method, no detectable trace of any of the analytes could be found in the other analytes that are present. Consistent relative peak shapes resulted from various dilutions of the eluent indicating no analytical interferences among the

components for any of the methods.

Columns, detector settings, and other specific details for each procedure will be given separately below.

3.1 Determination of Cr(III) Using HPIC-CG2 Columns

Several methods were developed for the analysis of Cr(III) and Cr(VI) in the presence of each other, and for Cr(III) and Fe(III) in the presence of Cr(VI). These methods follow in sections 3.1.1 - 3.1.4.

3.1.1 Determination of Cr(III) Using HPIC-CG2
Columns with A.A. Detection

This is a procedure for the analysis of Cr(III) in the presence of Cr(VI) by cationic separation using coupled ion chromatography and atomic absorption detection. Conditions were:

column:	Dionex CG2 cation separator
detector setting:	357.9 nm (absorbance)
eluent flow rate:	2.3 ml/min.
injection loop:	200 ul
eluent 1:	.100 M potassium chloride,
	.075 M sulfuric acid and

.050 M hydrochloric acid

eluent 2:   .02 M Cu(II) (copper sulfate)

signal processing: peak height

sample treatment: eluent dilution was useful

Chemicals used were:

Mallinckrodt: potassium chloride, sulfuric

acid, hydrochloric acid

EM Science: Cr(III) chloride, Zn(II)

nitrate, copper (II) sulfate

J.T. Baker: potassium chromate

3.1.2 Determination of Cr(III) Using HPIC-CG2 Columns with On-line Post Column Complexation with PAR

This is a procedure for determining Cr(III) in the presence of Cr(VI) using the same column, flow rate, injection loop, and signal processing as 3.1.1 but simultaneously using the filter and diode array type detectors. Also, a post column reactor (PCR) and a thermostatic bath heated reaction coil (80 degrees Celsius) was used for online post column PAR derivatization. After derivatization, a pH= 6.0 is necessary for complex stability and this requires no treatment of neutral samples or standards. Samples and

standards that are not neutral must be treated with hydrochloric acid or sodium hydroxide to a pH= 7.0 before derivatization. Condition were:

detector settings:	520nm, 1.0 AUFS (both)
eluent 1:	.100 M potassium chloride, .075 M sulfuric acid, and .050 M hydrochloric acid, adjusted to pH= 4.8 with LiOH
eluent 2:	.02 M Cu(II) (copper sulfate, same pH)
PCR reagent flow rate:	0.6 ml/minute
PCR reagent:	.0004 M PAR in 3 M ammonium hydroxide, and 1 M acetic acid

Many of the chemicals used in 3.1.1 were used here but in addition:

Fluka:	PAR, lithium hydroxide
EM Science:	ammonium hydroxide, acetic acid

3.1.3 Determination of Cr(III) and Fe(III)
Using HPIC-CG2 Columns with Off-line
PAR Complexing

This method permits determination of Cr(III) and
Fe(III) in the presence of Cr(VI), using pre-column
derivatization. The same column, detectors, eluents,
reagents, derivatization pH's, and other conditions as
used for 3.1.2 were employed except that post-column,
online derivatization was replaced by pre-column,
offline derivatization using a hotplate. The chemicals
used in 3.1.2 were also used here. The sample and
25 ml of PAR solution above were added to a 250 ml
volumetric flask. Each solution was boiled for one
minute and injected.

3.1.4 Determination of Cr(III)
Using HPIC-AG4 Column with Off-line
EDTA Complexing

This is still another method for determining
Cr(III) in the presence of Cr(VI), but now using an
anion exchange column and suppressed conductivity
detection. Eluent sodium hydroxide is necessary to
deprotonate EDTA. The procedure for standards and
samples is to add to a 250 ml volumetric flask enough
Cr(III) to make a 1-100 ppm Cr(III) solution after
dilution. Before dilution, .5 g EDTA and .5 g sodium
carbonate are also added to the neutral standards and

samples. Samples and standards that are not neutral, must be treated with hydrochloric acid or sodium carbonate to a pH= 7.0 before performing the last step. At this point the pH is greater than 7.0 in the flask before dilution. The undiluted solution is heated 15 minutes at 85 degrees Celsius in a pre-heated convection oven. A blue color forms if no chromate is present and a green color forms if chromate is present. After cooling the solutions, they are diluted to volume, and injected. Specific conditions were:

column:	Dionex AG4 separator
detector settings:	30 uS
eluent flow rate:	2.3 ml/ min.
injection loop:	10 ul
regenerate:	sulfuric acid
regenerate flow rate:	2.1 ml/ min.
eluent:	.0030 M sodium carbonate, .0020 M sodium hydroxide
signal processing:	peak height

Many of the chemicals used in 3.1.3 were used here but in addition:

Fluka:	EDTA (disodium salt)
J.T. Baker:	chromic acid
Mallinckrodt:	sodium hydroxide, sulfuric acid, sodium carbonate,

hydrochloric acid, and

sodium bicarbonate

3.2 Separation of Aqua-Complexes of Iron

and Copper by HPIC-CG2 Column with A.A. Detection

This procedure is useful for the determination of
the aqua-complexes of copper and iron in the presence
of other complexes of these metals, as well as other
cations and anions. Except for the detectors and
eluents, conditions were similar to 3.1.1. The
conditions employed were as followed:

column:	Dionex CG2 cation separator
detector setting:	248.3 nm (Fe absorbance)
	224.8 nm (Cu absorbance)
eluent flow rate:	2.3 ml/min.
injection loop:	200 ul
Fe eluent 1:	.080 M potassium chloride,
	.060 M sulfuric acid, and
	.040 M hydrochloric acid
Fe eluent 2:	.02 M Cu(II) (copper sulfate)
Cu eluent 1:	.033 M potassium chloride,
	.025 M sulfuric acid, and
	.017 M hydrochloric acid
Cu eluent 2:	.02 M Fe(III) (iron sulfate)

signal processing: peak height

Additional chemicals not used in 3.1.1 were:

Mallinckrodt:	sodium carbonate, potassium ferrocyanide
MCB:	ferrous ammonium sulfate, sodium cyanide, copper cyanide, and potassium ferricyanide
EM Science:	sodium hydroxide, zinc nitrate
J.T. Baker:	copper chloride, copper sulfate, and undried ferric chloride

3.3 Separation of Fe(II) and Fe(III)
Using HPIC-CG2 Column with On-line PAR Complexation

This is a means for the analysis of Fe(II) and Fe(III) in chromium and cyanide plating solutions, using uv-visible detection, and post-column derivatization. Two alternate eluents were used for the analysis of Fe(II) and Fe(III) in chromium and cyanide plating solutions. UV-visible detection and post column derivatization were employed as in 3.1.2. The iron compounds used were given in 3.2.1.

Fe eluent 1:	.080 M potassium chloride, .060 M sulfuric acid, and .040 M hydrochloric acid

and as above, adjusted to
pH= 4.3 with lithium hydroxide

Fe eluent 2:   .02 M Cu(II) (copper sulfate,
same pH)

3.4 Methods For the Separation of Copper

Two methods for copper in plating solutions were
developed using uv-visible and conductivity detection.
Both involved derivatization, but one used a cation
and the other an anion column. These methods follow
in sections 3.4.1 - 3.4.2.

3.4.1 Separation of Cu(II) Using HPIC-CG2 Column with On-line PAR Complexation

This section describes the analysis of Cu(II) in
chromium and cyanide plating solutions, using cationic
separation, uv-visible detection, and post-column
derivatization. Two alternate eluents were used. This
procedure is the same as in 3.3.1 except for the
eluent. Copper compounds used were given in 3.2.1.

Cu eluent 1:   .033 M potassium chloride,
.025 M sulfuric acid, and
.017 M hydrochloric acid

Cu eluent 2:   and as above, adjusted to
a pH= 4.3 with lithium hydroxide
.02 M Fe(III) (iron sulfate,
same pH)

3.4.2 Determination of Cu(II) Using HPIC-AG4 Column with Off-line EDTA Complexation

This is a method for determining Cu(II) in chromium plating, cyanide plating and polish solutions using the same procedure as 3.1.4 except that no pre-heating was required to form the complex. The procedure for making the solution was to place in a 100 ml volumetric flask less than 50 ppm total reactive metals and add 1 ml of .025 M EDTA to the neutral standards and samples. The solution was mixed and diluted to volume for injection. Samples and standards that are not neutral must be treated with hydrochloric acid or sodium carbonate to a pH= 7.0 before performing the last step. At this point the pH is greater than seven in the flask before dilution. Copper compounds employed were given in 3.2.

3.5 Separation of Cyano-Complexes

Two methods for determining iron and copper
cyanide complexes were developed, applicable to
copper and cadmium plating solutions. These methods
follow in sections 3.5.1 - 3.5.2.

3.5.1 Determination of Cyano-Complexes Using MPIC Column with A.A. Detection

This method is for the determination of ·iron and
copper cyanide complexes in the presence of their aqua-
complexes using MPIC anionic separation and atomic
absorption detection. The procedure differs from 3.2
only in the eluent chemicals and the separator column.
The eluent and column used were:

column:	Dionex MPIC anionic separator
eluent:	.020 M tetrabutyl ammonium hydroxide (TBOH), .0005 M sodium carbonate, and 30% acetonitrile

The differing chemicals used were:

Dionex:	tetrabutyl ammonium hydroxide
MCB:	acetonitrile, cadmium cyanide

3.5.2 Determination of Iron Cyano-Complexes Using MPIC Column with Conductivity Detection

This procedure allows determination of Fe(II) and Fe(III) cyanide complexes in cyanide plating solutions using MPIC anionic separation and suppressed conductivity detection. This procedure differs from 3.5.1 only in the use of a conductivity detector set at 30 uS.

3.6 Determination of Free Cyanide By Fe(III) Complexing Using MPIC Column and Conductivity Detection

This procedure allows the determination of free cyanide in copper and cadmium cyanide plating solutions by Fe(III) complexing, MPIC anionic separation and suppressed conductivity detection. Except for Fe(III) addition to the sample, this procedure is the same as 3.5.2.

3.7 Determination of Anions by HPIC-AG4 Column

Two methods for determining anions in metal finishing solutions were investigated. These methods follow in sections 3.7.1 - 3.7.2. The first of these is concerned with some complications arising in ar

established procedure.

3.7.1 Effects of pH on the
Determination of Anions by HPIC-AG4 Column

The following is the experimental conditions used in the analysis of anions in metal finishing solutions using new and old AG4 columns.

column:	Dionex AG4 separator
detector settings:	30 uS (conductivity)
	357.9 nm (Cr, A.A.)
	440 nm, .01 AU (uv-visible)
chemical suppression:	fiber suppressor module
eluent flow rate:	2.3 ml/min.
injection loop:	10 ul
regenerate:	sulfuric acid
flow rate (regenerate):	2.1 ml/min.
eluent 1:	.00300 M sodium carbonate (chromic acid type)
eluent 2:	.00100 M sodium carbonate (oxalic acid type)
signal processing:	peak height

Concentrations of injected standard solutions using a 10 ul injection loop instead of the normal 100 ul injection loop were:

chromium plating solutions: 10 ppm sulfuric acid,

                                1000 ppm chromic acid

polish solutions: 288 ppm phosphoric,

                                353 ppm sulfuric acid

anodize/ hardcoat solutions:

                                353 ppm sulfuric acid

                                72 ppm oxalic acid

Many of the chemicals used in 3.1.3 were used here but
in addition:

J.T. Baker: sodium carbonate; chromic,

                        sulfuric and oxalic acids

Mallinckrodt: sodium hydroxide, potassium

                        chromate, sodium chromate,

                        sodium sulfate, potassium

                        oxalate, sodium phosphate,

                        potassium phosphate,

                        potassium sulfate, sulfuric

                        acid, hydrochloric acid, and

                        phosphoric acid

3.7.2 Determination of Nitrate and Nitrite
in Metal Finishing Solutions

This experimental procedure for the determination
of nitrate and nitrite in chromium plating and polish

solutions uses the same conditions and chemicals as 3.7.1 with the exception of the following:

J.T. Baker: sodium nitrate, sodium
             nitrite

3.8 Determination of Ethylene Glycol Degradation Products in Metal Finishing Solutions

The following is the experimental procedure for the analysis of degradation products of ethylene glycol in chromium plating and polish solutions by exclusion separation and conductivity detection:

column:	Dionex HPICE-AG1 separator
detector settings:	10 uS (conductivity)
chemical suppression:	ISC column type
eluent flow rate:	1.0 ml/min.
injection loop:	100 ul
eluent:	.00100 M hydrochloric acid
signal processing:	peak height

Additional chemicals not used in 3.7.1 were:

J.T. Baker: hydrochloric acid

Fluka: ethylene glycol

3.9 Automated and Online Analysis of Metal Finishing Solutions

The procedure for an on-line, automated method for the determination of anions by ion chromatography follows the conditions of 3.7.1 but with the inclusion of the controller and dilution modules. Sample preparation time, handling, and attention is minimized by this method.

PART 4
RESULTS AND DISCUSSION

The methods described in the following section represent a number of practical analytical procedures for the analysis of metal finishing solutions of various kinds. It will be seen in some cases that several methods are described for a particular species. This has been done in part to provide for flexibility in choosing methods that can avoid separation complications in special cases, and also minimize restrictions on the detectors and columns that can be employed. Analysts with a limited choice of columns and detectors may still find a procedure here that can be used.

Results are given in such a way as to show their quantitative applicability, and at the same time are analyzed in terms of the standard chromatographic

parameters.

Errors are given in either standard deviation or relative standard deviation (percent) units as indicated and they are precision errors.

Throughout this report, half base widths (HW) are used instead of total widths for comparing resolution of unsymmetrical (tailing, etc.) and/or unequal peaks using equation 9. When compared peaks were nearly symmetrical and equal, resolution equations 9 and 10 gave the same values. As peaks become less symmetrical and less equal, equation 12 proved unreliable for calculating the number of column theoretical plates and this gives incorrect resolution values for equation 10. For symmetrical peaks, equation 12 gives about $N = 500$ plates for a new AG4 column with $L = 50$ mm and this is the number of plates that Dionex quotes in its specifications. From equation 14, the HETP equals about 0.1 mm and this also is in agreement with Dionex's data (14).

4.1 Determination of Cr(III) Using HPIC-CG2 Columns

Many methods have been developed for the estimation of Cr(III) using anionic and cationic separation. The detectors that were used for Cr(III)

were atomic absorption, uv-visible, and conductivity types. The atomic absorption type was the most specific requiring no further complexing while the the other two types of detectors were much more portable but required re-complexing of the Cr(III) complex.

4.1.1 Determination of Cr(III) Using HPIC-CG2 Columns with A.A. Detection

Presented here is a quick, specific, and precise method for the analysis of trivalent chromium complexes in the presence of hexavalent chromium by cation separation using coupled ion chromatography/ atomic absorption detection. The major application is for the analysis of chromium plating solutions. These are made up of Cr(VI), but some Cr(III) is produced during the electrolysis and can negatively effect plate properties and plating efficiency (67, 68). In an operating system, the hexavalent to trivalent chromium ratio varies from about 25-250 to 1. In the past, complex sample treatment and uv-visible estimation have been used, but the methods are time consuming and high in error. This method can easily and quantitatively analyze ppm level trivalent chromium in the presence of very high concentrations of hexavalent chromium and is

also substantially more precise than the tedious,
classical filtration methods in which the results are
the difference of two large numbers.

For the atomic absorption detector, the published
detection limit is .005 AAU (atomic absorption units)
and is linear to about .250 AAU according to Perkin-
Elmer instrument data. For this detector, 100
integrator units (IU) equals .010 AAU. The detection
limits and linearity range apply to the solution
entering the detector; this will be less than the
injected solution concentration values as a result of
chromatographic band broadening. This broadening
increases with increased retention time.

Table 5 shows the chromatographic results. The
number below the height (H) or retentions time (RT)
value is the error for the above value.

In Table 5, all Cr(III) runs fall in the linear
working range and have an acceptable level of error for
quantitative work. The standard Cr(III) originates
from chromium chloride and forms a hexa-aqua
chromium (III) complex when dissolved in water (67).

The Cr(VI) is introduced as chromic acid and forms
chromate which is not retained on the cation separator
column as shown in Table 5. Sodium chromate and
potassium chromate can be used instead of chromic acid,

Table 5. Chromatographic Data For Cr(III) and Cr(VI) Using HPIC-CG2 Column with A.A. Detection

Cr(III) (ppm)	Cr(VI) (ppm)	RT Cr(III) (min)	H Cr(III) (AAU)	RT Cr(VI) (min)	H Cr(VI) (AAU)
4	–	2.40 (.02)	.035 (.001)	–	–
8	–	2.42 (.01)	.067 (.001)	–	–
12	–	2.42 (.01)	.108 (.004)	–	–
20	–	2.40 (.01)	.174 (.007)	–	–
–	4	–	–	.48 (.01)	.131 (.003)
–	8	–	–	.48 (.01)	.260 (.005)
–	12	–	–	.48 (.01)	.394 (.009)
–	20	–	–	.48 (.01)	.793 (.016)
4	4	2.41 (.01)	.034 (.001)	.48 (.01)	.130 (.003)
4	520	2.42 (.01)	.035 (.001)	.48 (.01)	off-scale
–	520	–	–	.48 (.01)	off-scale

with identical results. In acid conditions some chromate dimerizes to dichromate. Because this detector is quite specific for chromium, this method could be used to quantify Cr(VI) as well as Cr(III); however there is no retention of Cr(VI), and other non-chromium species which elute with the solvent front, possibly interfering through atomic absorption matrix effects. This would have to be considered in the analysis of an unknown.

A typical chromium plating solution must be diluted in order to have concentrations that will be within the quantitative range of this technique. The second to the last run of Table 5 is a chromium plating solution standard with standard Cr(III) added as shown, while the last run shows the chromium plating standard alone. For a chromium plating solution with 25 to 250 times less Cr(III) than Cr(VI), it is difficult to determine both in the same run since they require much different dilutions and could not both be simultaneously in the linear working range of the AA detector. Determination from two separate runs is still possible with different dilutions. Dilution is determined solely by the requirement that the aspirated AA solution gives between .005-.250 AAU for chromium.

The retention times are 29 and 145 seconds for

chromate and Cr(III) respectively. Twenty-nine seconds represents the time required for the solvent to run through the system, because anions are not retained; this is the void volumn. The capacity factor (k') is 4.0 for the Cr(III). The half baseline width (HW) and the resolution (R) are calculated and presented in Tables 6 and 7 respectively. Calculations used equations 6, 9, 10, 11 and 12. These data are indicative of the quality of the chromatography for the Cr(III)/ Cr(VI) system. A factor called selectivity (a) can not be calculated here since it would require a k' for Cr(VI) which can not be obtained since this is a non-retained peak (NRP).

As mentioned, half base widths are used in equations 9 and 12 and must be multiplied by two in order to be used in either equation. Again the use of half widths (HW) is due to unsymmetrical peak shapes. There are three kinds of half widths, right (RW), either (EW) and left (LW) types. The choice is determined by peak shape.

The capacity factor is in the ideal range of 2-12. Since R's greater than 1.5 are considered baseline resolution, the separation is very good for all runs made.

The data in these Tables are for .02 M Cu(II)

Table 6. Half Width Data For Cr(III)/Cr(VI)

Ion	Conc (ppm)	Left Base Half Width (sec)	Right Base Half Width (sec)
Cr(VI)	20	-	6
Cr(VI)	520	-	12
Cr(III)	20	54	-

Table 7. Resolution (R) Values For Cr(III)/Cr(VI)

R	Cr(III) Conc (ppm)	Cr(VI) Conc (ppm)
1.9	20	20
1.8	20	520

eluent (as copper sulfate) but it should be noted that 0.100 M potassium chloride, .075 M sulfuric acid, and 0.050 M hydrochloric acid; and .02 M Zn(II) eluent (as zinc nitrate) give relative results that are so similar that they have not been included.

This method is much more rapid, sensitive, precise, and specific than the classical titration procedure. This approach has obvious extensions to many other elements that have both cationic and anionic forms.

4.1.2 Determination of Cr(III) Using HPIC-CG2 Columns with On-line Post Column Complexation with PAR

This is another quick, sensitive, specific, and precise method for the analysis of Cr(III) in the presence of Cr(VI) by cation separation using ion chromatography with filter or diode array uv-visible detection. Again, the major application is for chromium plating solutions. This method can quantitatively analyze ppm levels of Cr(III) in high concentrations of Cr(VI) and as before is more precise than classical methods.

Data are given in Table 8, where each Cr(III)

Table 8. Chromatographic Results For

Cr(III) by HPIC-CG2 Columns with Online

Heating and PAR Complexing

Run	Cr(III) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	–	–	–	–
2	1	2.19 (.02)	.085 (.004)	2.38 (.03)	.08 (.01)
3	2	2.19 (.02)	.169 (.007)	2.38 (.03)	.16 (.01)
4	3	2.19 (.02)	.258 (.011)	2.38 (.03)	.24 (.01)
5	5	2.19 (.02)	.432 (.020)	2.38 (.03)	.39 (.01)

solution contains 10.0 ppm sulfuric acid and 1000 ppm chromic acid. The Table shows injected concentrations and each run is an average of six subruns.

The hexa-aqua Cr(III) is selectively retained by the separator column and complexed by PAR while the chromate is not retained or complexed. PAR metal complexes are cation type complexes and Cr(III) complexing is slow due to slow kinetics, but as the results show, is complete in the time available in the derivatizing column at the temperature used.

Table 8 shows analytical results of Cr(III) by this method. The data are well within the linear working range of the detectors which is less than 500 ppm for a species and the results have an acceptable level of quantitative error. The slightly different retention times and peak heights for the two detectors result from the fact that the diode array spectrophotometer followed the filter spectrophotometer in the flowstream, so that a larger time was required before the sample reached the diode array detector, allowing for more peak broadening. Experiments were performed with the two detectors in series for the purpose of duplicating the methods, but in practical applications, only one need be used. Normally, the filter type detector would be the choice, because it is

less expensive and gives equal quality results. The diode array detector would be useful to analyze interferences or for multiple wavelength analysis. In any event, the capacity factor k' has a value of 4.0 using results from the upstream detector.

The right half base width of the Cr(VI) peak was six seconds while the left half base width of the Cr(III) peak was 27 seconds for 1-5 ppm of each using the filter type detector. Thus, the resolution R is calculated to have a value of 3.2. The quantities here are the same as in section 4.1.1 and again they illustrate the quality of the chromatography. As before, Cr(VI) is the non-retained peak. For the same reasons as above, a cannot be calculated here either.

The capacity factor is in the ideal range of 2-12. Since R's greater than 1.5 are considered baseline resolution, the separation is again very good for all runs made.

For the Cr(III)-PAR complex:

$$PAR^- + Cr(III) \longleftrightarrow PAR\text{-}Cr(III)^{2+} \tag{59}$$
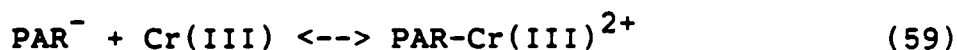
Since pH= 7.0 before derivatization, pH= 6.0 after derivatization, and the log of the formation constant for the PAR ligand is 27, then under these conditions the PAR-Cr(III) complex is totally formed in a practical sense, provided the time in the reactor

column is long enough for the reaction to go to completion. For 1 ppm Cr(III), e= 600000, c= .00002 M, b= .8 cm, and by equation 54, the calculated A= H= 10 AU at a retention time of 1 second. Since RT is inversely proportional to height, at about 100 seconds, the height H= .10 AU. The value of .10 AU compares very well with the measured value of .09 AU for Cr(III) in Table 8. The lower compared to the expected value from the calculation could result from incomplete complexation, but is in the range of the overall uncertainties and is not significant.

4.1.3 Determination of Cr(III) and Fe(III) Using HPIC-CG2 Columns with Off-line PAR Complexing

This is a quick, sensitive, specific, and precise method for the analysis of both Cr(III) and Fe(III) in the presence of Cr(VI) by cation separation using ion chromatography with filter or diode array UV-visible detection. Again, the major application is for chromium plating solutions. This method can quantitatively analyze ppm levels of Cr(III) and Fe(III) in very high concentrations of Cr(VI) and as before is more precise than classical methods.

The solutions used in Tables 9-10 all have 10.0 ppm sulfuric acid and 1000 ppm chromic acid in addition to trivalent chromium and iron cation complexes. The Tables show injected concentrations and each run is an average of six subruns.

The data are well within the linear working range of the detectors which is less than 500 ppm for a species and the results have an acceptable level of quantitative error. The hexa-aqua Cr(III) and Fe(III) are selectively retained by the separator column and complexed by PAR while the chromate is not retained or complexed. Again, the difference in retention times for the detectors is due to the diode array type being in series and down line from the filter type. Both detectors give suitable results. Cr(III) and Fe(III) can be determined in the same run as shown by the differences in retention times.

For the filter detector, the k' values were 1.8 and .58 for Cr(III) and Fe(III), respectively. The resulting a value is 3.1. For Cr(III) and Fe(III) for this same detector, the half base widths in seconds are 15 and 6, respectively. The resoluton for these two metals is 1.5. As before, Cr(VI) is the NRP and does not interfere. The capacity factor is only slightly out of the ideal range of 2-12 and is close to the 1.5

Table 9. Chromatographic Results For Cr(III)

Using an HPIC-CG2 Column with Offline PAR Complexing

Run	Cr(III) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	-	-	-	-
2	1	1.21 (.02)	.099 (.004)	1.43 (.03)	.09 (.01)
3	2	1.21 (.02)	.197 (.007)	1.43 (.03)	.16 (.01)
4	3	1.21 (.02)	.300 (.013)	1.43 (.03)	.25 (.01)
5	5	1.21 (.02)	.490 (.022)	1.43 (.03)	.40 (.01)

Table 10. Chromatographic Results For Fe(III)

Using an HPIC-CG2 Column with Offline PAR Complexing

Run	Fe(III) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	–	–	–	–
2	1	0.69 (.01)	.133 (.006)	0.87 (.02)	.10 (.01)
3	2	0.69 (.01)	.261 (.014)	0.87 (.02)	.21 (.01)
4	3	0.69 (.01)	.396 (.018)	0.87 (.02)	.31 (.01)
5	5	0.69 (.01)	.661 (.028)	0.87 (.02)	.52 (.01)

baseline resolution value required for good separation. Since a is larger than 1, the separation is acceptable.

The previously calculated value of .10 AU compares exactly with the measured value of .10 AU for Cr(III) in Table 9.

For Fe(III)-PAR complex:

$$PAR^- + Fe(III) \longleftrightarrow PAR\text{-}Fe(III)^{2+} \tag{60}$$

For Fe(III), the log of the formation constant of the PAR complex, 25, is close to that for Cr(III), and as calculated in 4.1.2, complexation is complete under the conditions used. The expected absorbance calculated as in the above section, is .13 AU for e= 800000 which compares exactly with the measured value of .13 AU for Fe(III) in Table 10. In the offline PAR derivatization, the measured and calculated absorbances agree exactly. The lower value found in the online case may suggest higher offline complexing percentage compared to the online case, but since the latter was within reasonable error limits, this is not established. However, use of higher flow rates in the online procedure would be riskly without futher checking.

4.1.4 Determination of Cr(III)

Using HPIC-AG4 Column with Off-line

EDTA Complexing

This is still another quick, sensitive, specific, and precise method for the analysis of Cr(III) in the presence of Cr(VI) by anion separation using ion chromatography with suppressed conductivity detection. Again, the major application is for chromium plating solutions. This method can quantitatively analyze ppm levels of Cr(III) in the presence of high concentrations of Cr(VI) and as before is more precise than classical methods. Unlike the other methods, it is based on the conversion of Cr(III) to an anionic complex.

Table 11 shows analytical results for Cr(III) by this method. The data are well within the linear working range of the detector as shown above and the uncertainty is well within the range necessary for quantitative use. The EDTA-Cr(III) complex is retained by the separator column but the other anions are retained differently.

The Cr(III) solutions reported in Table 11 also contain 10.0 ppm sulfuric acid and 1000 ppm chromic acid and each run is an average of six estimations.

Table 11. Determination of Cr(III) by Using

HPIC-AG4 Column with Offline EDTA Complexing

Run	Cr(III) (ppm)	RT (SCD) (min)	H (SCD) (uS)
1	0	-	-
2	4	0.61 (.01)	.022 (.001)
3	8	0.61 (.01)	.043 (.001)
4	12	0.61 (.01)	.065 (.002)
5	20	0.61 (.01)	.106 (.003)

The sulfate elutes at .95 minute' with a height of 1.18 uS and the chromate elutes at 2.35 minutes with a height of 8.82 uS. A 10 ul loop was used but if a 200 ul loop was substituted then the Cr(III) peak height increase proportionately but the other anion peak heights go offscale. It is difficult to determine Cr(VI) and sulfate in the same run as Cr(III) since Cr(III) has a very small peak while Cr(VI) has a very large non-linear peak.

The k' value is .28 for Cr(III). Since the only separation possible is with Cr(III) and the Cr(VI) in the NRP, the separation factor a cannot be calculated. The half base width in seconds of the non-retained peak and Cr(III) are 1 and 3, respectively. The resulting resolution for this system is 2.0.

The capacity factor is slighty out of the ideal range but resolution is again very good for all runs. The chemistry of the reaction is as follows:

$$Cr(III) + EDTA^{3-} + (HCO3)^{-} + Heat \longrightarrow$$
$$H(Cr(EDTA)(H2O)) + Base \longrightarrow$$
$$(Cr(EDTA)(OH^{-}))^{2-} \tag{61}$$
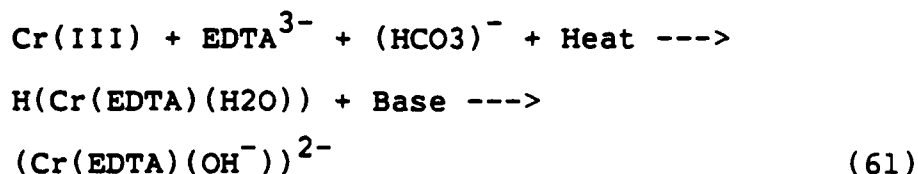
For a solution with only Cr(III) present and no chromate, the Cr(III) is green, violet and then blue as this reaction progresses (69). The Cr(III)-EDTA complex is formed at pH= 7-8 where 85-98% of the EDTA

is in the mono-protonated form before complexing, as the data in Table 12 will show. For this complex, the important equations are:
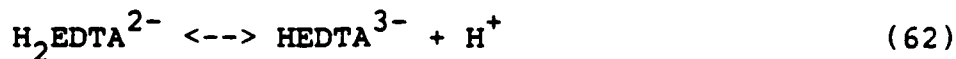
$$H_2EDTA^{2-} \longleftrightarrow HEDTA^{3-} + H^+ \tag{62}$$

$$Ka'' = (H^+)(HEDTA^{3-})/(H_2EDTA^{2-}) = 6.92 \times 10^{-7} \tag{63}$$

and pKa'' = 6.16. Substitution into equation 63 for Ka'' and the hydrogen ion concentration gives the ratio of more dissociated to less dissociated species at a given pH as Table 12 shows.

At pH = pKa'' = 6.16, the hydrogen ion concentration equals Ka'' = 0.000692 mM and the ratio in Table 12 is one.

The log of the formation constant for the EDTA-Cr(III) complex is 23 and under these conditions the complex can be considered totally formed for all practical purposes.

It may be noted that it is not possible to perform the complexation step online, first because the line in the reactor coil is too short, and also because it is impossible due to the high pressure to put the PCR before the column.

4.2 Separation of Aqua-Complexes of Iron and Copper by HPIC-CG2 Column with A.A. Detection

Table 12. EDTA Ka'' Data

pH   log $(HEDTA^{3-}/H_2EDTA^{2-})$

pH	log $(HEDTA^{3-}/H_2EDTA^{2-})$
1	-5.16
2	-4.16
3	-3.16
4	-2.16
5	-1.16
6	-0.16
7	0.84
8	1.84
9	2.84
10	3.84
11	4.84
12	5.84
13	6.84
14	7.84

This is a specific method for aqua-iron and copper complex analysis in the presence of other iron and copper cation complexes, anionic iron and copper complexes, other anions, and other cations by employing a cation separator column and ion chromatography with online atomic absorption detection. The major applications involve chromium plating, chromium polish, and cyanide plating solutions where aqua-complexes of iron and copper are harmful to plating properties, and methods for determining them are important. This method provides fast and quantitative results to ppm detection levels for these complexes and gives substantial improvement over classical methods.

In this procedure, a cation separator column is used for separation of positive aqua-complexes while negatively charged species elute in the void volume. Atomic detection is used after ionic separation of these complexes. The high concentrations of plating and polishing solution anions and cations give no interferences with the analysis of iron and copper complexes since AA detection is very specific for the selected element. In the iron separation, Fe(II) or Fe(III) cyanide complexes can be used to mark the void volume. For iron, the AA detector has a detection limit of .005 AAU and is linear to .180 AAU; while for

copper, these values are .006 AAU and .250 AAU,
respectively. Again, because of band broadening, the
actual injected concentrations can be higher. Tables
13-15 give the iron and copper data. The actual
species present in aqueous solution are hexa-aqua
iron (II), hexa-aqua iron (III), hexa-cyano iron (II),
hexa-cyano iron (III), hexa-aqua copper (II), and
tetra-cyano copper (I) (67, 70, 71).

In Table 13, showing results for the iron system,
all aqua-iron complex runs fall in the linear working
range of the detector and have minimal quantitative
error except runs 6-8 which could be made to fall
within the linear range with further dilution. The
difference in retention times of Fe(II) and Fe(III)
aqua-complexes in Table 13 gives baseline resolution.

The number below the height (H) or retentions time
(RT) is the experimental error for the above value.
Table 14 shows that Fe(II) and Fe(III) cyanide
complexes both elute at or near the void volume for
the same conditions as in Table 13. This detector is
specific for iron and this method could be used to
quantify total anionic iron complexes, although there
is no retention of these anionic complexes and other
non-iron species elute at the same time, giving the
possibility of interference through matrix effects.

Table 13. Determination of Aqua-Iron Complexes Using HPIC-CG2 Column with A.A. Detection

Fe(II) (ppm)	Fe(III) (ppm)	RT Fe(II) (min)	H Fe(II) (AAU)	RT Fe(III) (min)	H Fe(III) (AAU)
4	-	0.85 (.02)	.119 (.004)	-	-
8	-	0.85 (.02)	.245 (.009)	-	-
12	-	0.85 (.02)	.377 (.015)	-	-
20	-	0.85 (.02)	.613 (.024)	-	-
-	4	-	-	1.64 (.03)	.032 (.001)
-	8	-	-	1.64 (.03)	.055 (.002)
-	12	-	-	1.66 (.01)	.106 (.003)
-	20	-	-	1.64 (.02)	.139 (.006)
4	4	0.83 (.02)	.118 (.005)	1.64 (.02)	.032 (.001)

Table 14. Determination of Iron Cyanide Complexes

Using HPIC-CG2 Column with A.A. Detection

Fe(II) (ppm)	Fe(III) (ppm)	RT Fe(II) (min)	H Fe(II) (AAU)	RT Fe(III) (min)	H Fe(III) (AAU)
4	–	0.46 (.01)	.164 (.006)	–	–
8	–	0.46 (.01)	.368 (.013)	–	–
12	–	0.46 (.01)	.515 (.019)	–	–
20	–	0.46 (.01)	.821 (.030)	–	–
–	4	–	–	0.48 (.02)	.160 (.007)
–	8	–	–	0.48 (.02)	.309 (.016)
–	12	–	–	0.48 (.02)	.438 (.020)
–	20	–	–	0.48 (.02)	.754 (.028)

Table 15. Determination of Copper Complexes

Using HPIC-CG2 Column with A.A. Detection

Cu(II) (ppm)	Cu(I) (ppm)	RT Cu(II) (min)	H Cu(II) (AAU)	RT Cu(I) (min)	H Cu(I) (AAU)
4	–	1.78 (.01)	.092 (.003)	–	–
8	–	1.78 (.02)	.180 (.005)	–	–
12	–	1.74 (.01)	.246 (.011)	–	–
20	–	1.74 (.01)	.414 (.015)	–	–
–	4	–	–	0.47 (.01)	0.357 (.011)
–	8	–	–	0.48 (.02)	0.712 (.021)
–	12	–	–	0.48 (.01)	1.058 (.033)
–	20	–	–	0.48 (.01)	1.711 (.060)
4	4	1.74 (.02)	.090 (.002)	0.48 (.01)	0.352 (.010)

In Table 15, which gives the copper results, all of the given aqua-copper complex runs fall within the linear working range of the detector and have an acceptable level of quantitive error except the fourth run which could be made linear with further dilution. Table 15 also shows that the copper (I) cyanide complex elutes at the void volume for the same conditions as aqua-copper. This detector is specific for copper and this method could be used to quantify this anionic copper complex, but there is no retention of this anionic complex and other non-copper species elute at the same time, with again the possibility of interference. The ninth run in Tables 13 and 15 is mixtures of the two aqua-complexes and shows agreement with the unmixed standards.

The k' values for Fe(II) and Fe(III) are .82 and 2.5, respectively. The resulting a value is 3.0. The non-retained peak consists of anionic cyanide complexes. The half base widths in seconds for Fe(II) and Fe(III) are 6 and 21, respectively. The resolution of the two iron complexes is 1.7.

The capacity factor is slighty out of the ideal range but resolution is again very good for all runs due to a large selectivity value for aqua-iron.

The k' value for Cu(II) is 2.7. Again, since

separation is only possible with the non-retained peak, no a value is possible. The half base width in seconds of the non-retained peak and Cu(II) are 3 and 15, respectively. The resulting resolution for this system is 4.3.

The capacity factor is within the ideal range and resolution is again very good for all copper runs.

The data in Tables 13-15 are for Fe(III) or Cu(II) sulfate type eluent but it should be noted that the KCl type eluent, potassium chloride type eluent and the Zn(II) type eluent give relative results so similar that tables for these other eluents have not been included.

The error of this method is quantitatively acceptable. This method is much more rapid, sensitive, precise, and specific than the classical titration method. This method has obvious extensions for many other elements that have at least 2 ionic forms.

4.3 Separation of Fe(II) and Fe(III)
Using HPIC-CG2 Column with On-line PAR Complexation

This is another quick, sensitive, specific, and precise method for the analysis of Fe(II) and Fe(III) in chromium plating, cyanide plating, and polish

solutions. A cation separator column and filter or
diode array uv-visible detection was used. This method
can quantitatively analyze ppm level of Fe(II) and
Fe(III) and is an improvement over classical methods.
Tables 16-17 show analytical results of Fe(II) and
Fe(III) by this method. The data are well within the
linear working range of the detectors which is less
than 500 ppm for a species and the results have a
minimium level of quantitative error. The hexa-aqua
Fe(II) and Fe(III) species are retained by the
separator column and complexed by PAR while the anions
are not retained. This complexation can be performed
online.

In terms of detector response, the previously
calculated value of .13 AU compares well with the
measured value of .11 AU for Fe(III) in Table 17.

For the Fe(II)-PAR complex:

$$PAR^- + Fe(II) \longleftrightarrow PAR\text{-}Fe(II)^+ \tag{64}$$
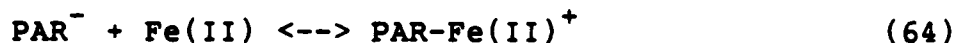
For Fe(II), the log of the formation constant of the
PAR complex, 18, is close to that for Cr(III), and as
calculated in 4.1.2, complexation is complete under the
conditions used. The expected absorbance calculated as
in the above section, is .08 AU for e= 500000, which
compares very well with the measured value of .07 AU
for Fe(II) in Table 16.

Table 16. Determination of Fe(II) Using HPIC-CG2
Column with Online PAR Complexation

Run	Fe(II) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	-	-	-	-
2	1	0.78 (.02)	.065 (.002)	0.98 (.03)	.05 (.01)
3	2	0.78 (.02)	.128 (.006)	0.98 (.03)	.10 (.01)
4	3	0.78 (.02)	.195 (.010)	0.98 (.03)	.15 (.01)
5	5	0.78 (.02)	.328 (.020)	0.98 (.03)	.26 (.01)

able 17. Determination of Fe(III) Using HPIC-CG2
Column with Online PAR Complexation

Run	Fe(III) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	-	-	-	-
2	1	1.52 (.03)	.110 (.006)	1.79 (.04)	.09 (.01)
3	2	1.52 (.03)	.226 (.010)	1.79 (.04)	.18 (.01)
4	3	1.52 (.03)	.334 (.015)	1.79 (.04)	.28 (.01)
5	5	1.52 (.03)	.560 (.026)	1.79 (.04)	.48 (.02)

Each sample of Fe(II) and Fe(III) also contains 288 ppm phosphoric and 353 ppm sulfuric acid. Tables 16-17 show injected concentrations and each run is an average of six subruns.

For the filter type detector, the capacity factor data for Fe(II) and Fe(III) are .81 and 2.5, respectively. The resulting separtion factor is 3.1. The half base widths in seconds for Fe(II) and Fe(III) are 6 and 15, respectively. The resolution of these two iron complexes is 2.1. The non-retained peak contains anions.

The capacity factor is slighty out of the ideal range but resolution is again very good for all runs due to large selectivity values. The retention time relationship between the filter and diode array type detectors is again due to plumbing.

4.4 Methods For the Separation of Copper

Sections 4.4.1 - 4.4.2 give methods for the determination of Cu(II) by HPIC.

4.4.1 Separation of Cu(II) Using an HPIC-CG2 Column with On-line PAR Complexation

This is another quick, sensitive, specific, and
precise method for the analysis of Cu(II) in chromium
plating, cyanide plating, and polish solutions. A
cation separator column is used with filter and/ or
diode array ultraviolet-visible detection. This method
can quantitatively analyze ppm levels of Cu(II) and is
more precise than classical methods. This method is
for online analysis, in contrast to the offline PAR
complexation method above.

Table 18 shows analytical results of Cu(II) by
this method. The data are well within the linear
working range of the detectors which is less than
500 ppm for a species and the results have an
acceptably low level of quantitative error. The hexa-
aqua Cu(II) complex is retained by the separator column
and complexed by PAR after elution while the anions are
not retained.

For the Cu(II)-PAR complex:

$$PAR^- + Cu(II) \longleftrightarrow PAR\text{-}Cu(III)^+ \tag{65}$$
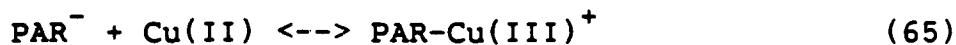
For Cu(II), the log of the formation constant of the
PAR complex, 21, is close to that for Cr(III), and as
calculated in 4.1.2, complexation is complete under the
conditions used. The expected absorbance calculated
as in the above section, is .13 AU for e= 800000,
which compares well with the measured value of .11 AU

Table 18. Determination of Cu(II) Using an HPIC-CG2
Column with Online PAR Complexation

Run	Cu(II) (ppm)	RT (FD) (min)	H (FD) (AU)	RT (DAD) (min)	H (DAD) (AU)
1	0	-	-	-	-
2	1	1.64 (.02)	.106 (.004)	1.83 (.03)	.10 (.01)
3	2	1.64 (.02)	.218 (.010)	1.83 (.03)	.20 (.01)
4	3	1.64 (.02)	.330 (.017)	1.83 (.03)	.29 (.01)
5	5	1.64 (.02)	.552 (.022)	1.83 (.03)	.49 (.02)

for Cu(II) in Table 18.

The solutions for each run of Cu(II) contain 288 ppm phosphoric and 353 ppm sulfuric acid. Table 18 shows injected concentrations and each run is an average of six subruns.

The following chromatographic information is for the filter type detector although there is a direct relationship to the diode array detector as stated above. The k' value for Cu(II) is 2.8 and since the only separation possible is with non-retained peak anions, the separation factor cannot be calculated. The half base widths in seconds are 3 and 15 for the Cu(I) and Cu(II) complexes, respectively. The associated resolution is 4.0.

The capacity factor is within the ideal range and resolution is again very good for all runs.

## 4.4.2 Determination of Cu(II) Using an HPIC-AG4 Column with Off-line EDTA Complexation

This is still another quick, sensitive, specific, and precise method for the analysis of Cu(II) using ion chromatography with suppressed conductivity detection. Again, the major applications are for chromium plating, cyanide plating, and polish solutions

using an anionic column. This method can
quantitatively analyze ppm levels of Cu(II) and is more
precise than classical methods.

Table 19 shows analytical results of Cu(II) by
this method. The data are well within the linear
working range of the detector as shown above and both
the data and error are quantitative. The EDTA-Cu(II)
complex is retained by the separator column but the
other anions are retained differently.

The data in Table 19 are for Cu(II) but in
addition each run has 10.0 ppm sulfuric acid and
1000 ppm chromic acid. Table 19 shows injected
concentrations and each run is an average of six
subruns. The Cu-EDTA complex is sought and is easy to
form (69).

The sulfuric acid elutes at .96 minute with a
height of 1.19 uS and the chromic acid elutes at 2.38
minutes with a height of 8.76 uS. A 10 ul loop was
used but if a 200 ul loop was substituted then the
Cu(II) peak height increases proportionately while the
other anion peak heights go offscale.

The k' value for Cu(II) is 1.7. Again, since
separation is only possible with the non-retained peak,
no a value is possible. The half base width in seconds
of the non-retained peak and Cu(II) are 3 and 15,

Table 19. Determination of Cu(II) Using an HPIC-AG4
Column with Offline EDTA Complexation

Run	Cu(II) (ppm)	RT (SCD) (min)	H (SCD) (uS)
1	0	–	–
2	4	1.31 (.02)	.017 (.001)
3	8	1.31 (.02)	.033 (.001)
4	12	1.31 (.02)	.048 (.002)
5	20	1.31 (.02)	.080 (.004)

respectively. The resulting resolution for this system is 2.8. The non-retained peak contains cations.

The capacity factor is within the ideal range and resolution is again very good for all runs.

For the Cu(II)-EDTA complex:

$$HEDTA^{3-} + base + Cu(II) <-->$$

$$Cu(II)(EDTA)(OH^-)^{3-} \qquad (66)$$
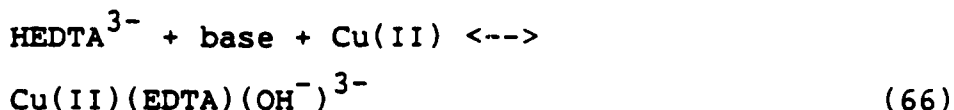
The Cu(II)-EDTA complex is formed at pH= 7-8 where 85-98% of the EDTA is in the the mono-protic form, before complexing, as shown for EDTA in the case of Cr(III)-EDTA above. The log of the formation constant for the EDTA-Cu(II) complex is 19 and under these conditions the complex can be considered totally formed for all practical purposes.

It is noted that this method can not be performed online with post-heat because the CG2 column uses acidic eluent, the AG4 column gives no retention, and the time in the reactor coil is too short to form the complex sought. Also, it is impossible due to the high pressure to put the post column reactor before the separator column.

4.5 Separation of Cyano-Complexes

Sections 4.5.1 - 4.5.2 give methods for cyano-

complexes by MPIC.

4.5.1 Determination of Cyano-Complexes Using an MPIC Column with A.A. Detection

A rapid, sensitive, precise, and specific method is presented here for the analysis of iron and copper cyanide complexes in the presence of iron and copper aqua-complexes by mobile phase ion chromatography with online AA detection. There are 2 major applications related to cyanide and aqua-complexes. One is to determine iron contamination in cadmium and copper cyanide plating solutions. This is generally of importance for the treatment and disposal stages. The other application is to determine the concentration distribution of copper cyanide and copper aqua-complexes in copper cyanide plating solutions in order to optimize concentrations for the plating process. Copper aqua-complexes interfere with the copper cyanide plating process (67). This method provides fast and quantitative results to ppm detection levels for these complexes and gives substantial improvement over classical methods.

In this procedure, a MPIC separator column is used for separation of negative cyano-complexes while

positively charged species elute in the void volume. Atomic detection is used after ionic separation of these complexes. The high concentrations of plating solution anions and cations give no interferences with the analysis of iron and copper complexes since AA detection is very specific for the selected element. Results are given in Tables 20-22. The actual species present in aqueous solutions are hexa-aqua iron (II), hexa-aqua iron (III), hexa-cyano iron (II), hexa-cyano iron (III), hexa-aqua copper (II), and tetra-cyano copper (I) (67, 70, 71). The hexa-cyano iron (II) and tetra-cyano copper (I) complexes are extremely stable in aqueous solution (71). The hexa-cyano iron (III) complex is a mild oxidizing agent and is labile to water substitution in aqueous solutions and may form penta-cyano mono-aqua iron (III) (71).

The k' values for Fe(II) and Fe(III) cyano-complexes are 2.3 and 3.2, respectively. The resulting a value is 1.4. The non-retained peak consists of cationic aqua-complexes. The half base widths in seconds for Fe(II) and Fe(III) are 6 and 12, respectively. The resolution of the two iron complexes is 1.6.

The capacity factor is almost within the ideal range and resolution is again good for all runs due to

Table 20. Determination of Iron Cyanide Complexes

Using MPIC column with A.A. Detection

Fe(II) (ppm)	Fe(III) (ppm)	RT Fe(II) (min)	H Fe(II) (AAU)	RT Fe(III) (min)	H Fe(III) (AAU)
4	–	1.60 (.03)	.042 (.002)	–	–
8	–	1.58 (.03)	.085 (.003)	–	–
12	–	1.58 (.03)	.132 (.004)	–	–
20	–	1.58 (.03)	.216 (.007)	–	–
–	4	–	–	2.06 (.03)	.031 (.002)
–	8	–	–	2.05 (.03)	.059 (.002)
–	12	–	–	2.04 (.03)	.088 (.003)
–	20	–	–	2.04 (.03)	.150 (.006)
4	4	1.58 (.03)	.041 (.001)	2.04 (.03)	.030 (.001)

Table 21. Determination of Iron-Aqua Complexes

Using MPIC column with A.A. Detection

Fe(II) (ppm)	Fe(III) (ppm)	RT Fe(II) (min)	H Fe(II) (AAU)	RT Fe(III) (min)	H Fe(III) (AAU)
4	-	0.48 (.01)	.201 (.007)	-	-
8	-	0.48 (.01)	.381 (.015)	-	-
12	-	0.48 (.01)	.590 (.021)	-	-
20	-	0.48 (.01)	.941 (.039)	-	-
-	4	-	-	0.48 (.01)	.198 (.006)
-	8	-	-	0.48 (.01)	.362 (.011)
-	12	-	-	0.48 (.01)	.537 (.016)
-	20	-	-	0.48 (.01)	.902 (.036)

Table 22. Determination of Copper Complexes

Using MPIC column with A.A. Detection

Cu(II) (ppm)	Cu(I) (ppm)	RT Cu(II) (min)	H Cu(II) (AAU)	RT Cu(I) (min)	H Cu(I) (AAU)
4	–	0.48 (.01)	0.348 (.012)	–	–
8	–	0.48 (.01)	0.667 (.025)	–	–
12	–	0.48 (.01)	1.037 (.033)	–	–
20	–	0.48 (.01)	1.722 (.065)	–	–
–	4	–	–	1.29 (.01)	.106 (.002)
–	8	–	–	1.29 (.01)	.210 (.007)
–	12	–	–	1.29 (.01)	.282 (.007)
–	20	–	–	1.29 (.01)	.476 (.018)
4	4	0.46 (.01)	0.350 (.009)	1.29 (.01)	.108 (.002)

good selectivity.

The k' value for Cu(I) is 1.7. Again, since separation is only possible with the non-retained peak, no a value is possible. The half base width in seconds of the non-retained peak and Cu(I) are 3 and 12, respectively. The resulting resolution for this system is 3.2. The non-retained peak contains cations.

The capacity factor is almost within the ideal range and resolution is again good for all runs.

In the iron separation, Fe(II) and Fe(III) aqua-complexes can be used to mark the void volume. For iron, the AA detector has a detection limit of 0.005 AAU and is linear to .180 AAU; and for copper, the AA detector has a detection limit of .006 AAU and is linear to .250 AAU. For a given concentration of a metal, as the retention time increases, the peak height decreases due to chromatographic band broadening so that the aspirated concentrations are less than the injected concentrations. At injection, the latter may be greater than the linearity range of the detector.

In Table 20, all cyano-iron complex runs fall in the linear working range of the detector and have an acceptable level of quantitative error except the fourth run which could be made linear with further dilution. Retention time differences of Fe(II) and

Fe(III) cyano-complexes in Table 20 give baseline
resolution for each. The ninth run in Table 20 is a
mixture of the two cyano-complexes and is in agreement
with the unmixed standards. The ninth run is an iron
contaminated copper or cadmium cyanide plating solution
in the treatment or disposal stage.

Table 21 shows that Fe(II) and Fe (III) aqua-
complexes both elute at or near the void volume for the
same conditions as in Table 20 and can be determined at
least in principle by this method. This detector is
specific for iron and this method could be used to
determine total cationic iron complexes, but there is
no retention of these cationic complexes and other non-
iron species elute at the same time giving possible
interferes.

In Table 22, all cyano-copper complex runs fall
within the linear working range of the detector and
have an acceptable level of quantitative error except
runs seven and eight which could be made linear by
further dilution. Table 22 also shows that the
copper (II) aqua-complex elutes at the void volume for
the same conditions as cyano-copper. Again,
quantitation of cationic copper is possible if non-
separated species do not interfere. The ninth run in
Table 22 is a mixture of the 2 copper complexes and is

in agreement with the unmixed standards; it is a copper
cyanide plating solution that is 50% low in cyanide.

This method is much more rapid, sensitive,
precise, and specific than the classical titration
method. This method has obvious extensions for many
other elements that have at least 2 ionic forms.

4.5.2 Determination of Iron Cyano-Complexes Using MPIC Column with Conductivity Detection

This is still another quick, sensitive, specific,
and precise method for the analysis of Fe(II) and
Fe(III) cyanide complexes where the major applications
are for cadmium and copper cyanide plating solutions.
An anionic MPIC column is used with suppressed
conductivity detection. This method can quantitatively
analyze ppm levels of these complexes and is more
precise than classical methods.

Conductance (G) was calculated by equation 49 for
10 ppm of each of the two important sodium salt
forms and E was taken from data in Table 3. For
sodium ferricyanide and sodium ferrocyanide, the
resulting conductance was 30 uS for each. The
conductances of the anions are low in their sodium form
and high in their acid form. Calculated G values are

for a retention time of one second and a height of x uS for any given anion. Since RT is inversely proportional to height, at y seconds, the height G= x/y uS. The value at 10 ppm of each salt compares well with the measured values in Tables 23-24.

Tables 23-24 show the measured results for these cyano-complexes in a cadmium plating solution. The data are well within the linear working range of the detector as shown above and the data are quantitative with acceptably small error. These complexes and other anions are retained by the column but the cations, including the cadmium, are not. This method can be performed online, unlike the classical methods that it replaces.

Tables 23-24 show injected concentrations and each run is an average of six subruns.

The k' values for Fe(II) and Fe(III) are 2.5 and 3.4, respectively. The resulting a value is 1.4. The half base widths in seconds for Fe(II) and Fe(III) are 6 and 12, respectively. The resolution of the two iron complexes is 1.6. The capacity factor is within the ideal range and resolution is again good for all runs due to good selectivity. The non-retained peak consists of cationic aqua-complexes.

Table 23. Determination of Fe(II)

Using MPIC Column with Conductivity Detection

Run	Fe(II) (ppm)	RT (SCD) (min)	H (SCD) (uS)
1	0	-	-
2	4	1.69 (.03)	2.6 (.1)
3	8	1.70 (.03)	5.4 (.1)
4	12	1.70 (.03)	8.0 (.2)
5	20	1.71 (.03)	13.2 (.3)

Table 24. Determination of Fe(III)

Using MPIC Column with Conductivity Detection

Run	Fe(III) (ppm)	RT (SCD) (min)	H (SCD) (uS)
1	0	–	–
2	4	2.15 (.03)	4.5 (.1)
3	8	2.16 (.03)	9.0 (.2)
4	12	2.16 (.03)	13.4 (.3)
5	20	2.18 (.03)	22.0 (.5)

4.6 Determination of Free Cyanide By Fe(III)
Complexing Using an MPIC
Column and Conductivity Detection

This is quick, sensitive, specific, and precise
method for the analysis of cyanide by Fe(III)
complexing where the major applications are for cadmium
and copper cyanide plating solutions. An anionic MPIC
column is used with suppressed conductivity detection.
This method can quantitatively analyze ppm levels of
this complex and is more precise than classical
methods. Amperometric detection of free cyanide can be
used to prove there is complete complexing (59).

Another method using iodide reagent and
conductivity detection can be used to detect free
cyanide; it has been used for cyanide analysis (72).
The reaction is:

$$I_2 + HCN \longleftrightarrow H^+ + I^- + ICN \qquad (67)$$
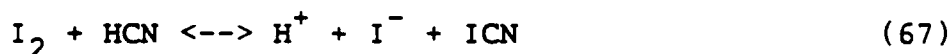
with Keq= 0.73. This reaction is very pH sensitive.

The method presented here is more specific and
interference-free than the iodide method for the
determination of free cyanide. This is due to AA
detection which is specific and nearly interference-
free while the iodide method requires very similar
standards and samples, and is not always possible to

achieve.

Table 25 shows the results from this method. The data are well within the linear working range of the detector as shown above and the data are quantitative · with an acceptably small error. This complex and other anions are retained by the column but the cations are not. This method can be performed online, unlike the classical methods that it replaces.

The data in Table 25 are for the iron (III) cyanide complex formed when Fe(III) in excess is added to a cyanide plating solution. Table 25 shows injected concentrations and each run is an average of six subruns.

The k' value for Fe(III) is 3.5. Again, since separation is only possible with the non-retained peak, no a value is possible. The half base width in seconds of the non-retained peak and Fe(III) are 3 and 12, respectively. The capacity factor is within the ideal range and resolution is again very good for all runs. The resulting resolution for this system is 6.7. The non-retained peak contains uncomplexed Fe(III) and other cations.

4.7 Determination of Anions by HPIC Using AG4 Columns

Table 25. Determination of Iron-Complexed Cyanide

Run	Cyanide (ppm)	Ferricyanide (ppm)	RT (SCD) (min.)	H (SCD) (uS)
1	0	0	-	-
2	.5	4	2.15 (.03)	4.5 (.1)
3	1.0	8	2.16 (.03)	9.0 (.2)
4	1.5	12	2.16 (.03)	13.4 (.3)
5	2.5	20	2.18 (.03)	22.0 (.5)

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Two methods for determining anions in metal finishing solutions were investigated. These methods follow in sections 4.7.1 - 4.7.2. The first of them does not represent a new procedure, but rather a study of difficulties arising in an established procedure that have not been recognized previously.

4.7.1 Effects of pH on the Determination of Anions by HPIC Using AG4 Columns

In the analysis of metal finishing solutions containing chromate, phosphate, sulfate, and oxalate by ion chromatography, peak heights and areas vary widely depending on the acid or base content of the injected sample. This is most evident for strongly retained ions. A similar composition of standards and samples is essential for quantitative results. Surprisingly, this problem does not seem to have been recognized in most published descriptions of this analytical technique. The effect is related to changes in the eluent strength during elution and separator column overloading where both are independent of the type of detector used.

Sulfate enhances plating performance while chloride at 2 g/l gives pitting and poor performance in

chromium plating solutions (27). It is therefore important to quantify these ions and ion chromatography is favored over wet methods because of speed and potential precision.

Although the quantity of material in a chromatographic peak is strictly proportional to peak area, the main focus of this discussion is on peak height since most ion chromatography data are presented that way in the literature. The variation of peak height (H), peak area (A), and retention time (RT) due to differences in the pH of the injected sample at a constant sample concentration are illustrated in Tables 26-29. However, it is also shown in the Tables that for runs that have baseline resolution and separation, the areas are not constant for constant concentrations. In fact, this pH effect of the sample forms a rather linear correlation between pH, peak heights and peak areas for the given systems in Tables 26-29 and is not just a change in peak height as the peak broadens or narrows.

For the given data, new columns refer to the columns that have been used for fewer than 50 runs and old columns represent those that have had 200-300 runs made on them. For the conductivity detector, peak height (H) and peak area (A) units are in uS and uS-

Table 26. Chromatographic Results for New Chromium
Plating Solutions Using AG4 Columns and Added HCl

N HCl	1	.1	.01	.001	0
RT NRP	-	.42	.42	.42	.42
RT Chloride	-	1.10	.67	.53	.53
RT Sulfate	-	-	-	.92	.92
	-	-	-	(.02)	(.02)
H "	-	-	-	1.02	1.18
	-	-	-	(.04)	(.04)
A "	-	-	-	3.03	3.51
	-	-	-	(.15)	(.16)
RT Chromate	-	2.68	2.15	1.96	1.96
	-	(.04)	(.03)	(.04)	(.03)
H "	-	5.26	6.36	8.78	8.82
	-	(.09)	(.09)	(.09)	(.16)
A "	-	200	246	338	339
	-	(12)	(13)	(19)	(18)

Table 27. Chromatographic Results for New Chromium
Plating Solutions Using AG4 Columns and Added NaOH

N NaOH	0	.001	.01	.1	1
RT NRP	.42	.42	.42	.42	.42
RT Hydroxide	.53	.53	.53	.53	.55
RT Sulfate	.92 (.02)	.92 (.02)	.92 (.02)	.92 (.02)	— —
H "	1.18 (.04)	1.18 (.03)	1.18 (.03)	1.17 (.04)	— —
A "	3.51 (.16)	3.51 (.15)	3.51 (.16)	3.45 (.16)	— —
RT Chromate	1.96 (.03)	1.96 (.03)	1.91 (.03)	1.84 (.03)	1.84 (.02)
H "	8.82 (.16)	8.80 (.12)	9.63 (.15)	11.5 (.18)	11.2 (.19)
A "	339 (18)	338 (20)	345 (19)	351 (20)	349 (21)

Table 28. Chromatographic Results for New Acid
Treatment Solutions Using AG4 Columns and Added HCl

N HCl	1	.1	.01	.001	0
RT NRP	-	.42	.42	.42	.42
RT Chloride	-	1.71	.93	.69	.68
RT Phosphate	-	-	1.78	1.78	1.78
	-	-	(.04)	(.03)	(.02)
H "	-	-	10.3	10.4	10.4
	-	-	(.2)	(.2)	(.2)
A "	-	-	86.6	88.1	88.1
	-	-	(5.9)	(5.9)	(6.0)
RT Sulfate	-	3.11	2.99	2.99	2.99
	-	(.02)	(.02)	(.02)	(.03)
H "	-	15.7	15.8	15.8	15.8
	-	(.3)	(.3)	(.3)	(.3)
A "	-	127	128	128	128
	-	(7)	(8)	(7)	(7)
RT Oxalate	-	-	4.80	4.80	4.80
	-	-	(.03)	(.03)	(.06)
H "	-	-	1.73	1.73	1.73
	-	-	(.04)	(.03)	(.04)
A "	-	-	25.0	25.0	25.0
	-	-	(1.6)	(1.6)	(1.6)

Table 29. Chromatographic Results for New Acid Treatment Solutions Using AG4 Columns and Added NaOH

N NaOH	0	.001	.01	.1	1
RT NRP	.42	.42	.42	.42	.42
RT Hydroxide	.68	.68	.68	.68	.90
RT Phosphate	1.78 (.02)	1.78 (.03)	1.72 (.02)	1.70 (.03)	1.70 (.02)
H "	10.4 (.20)	10.4 (.16)	10.6 (.15)	10.8 (.23)	10.7 (.26)
A "	88.1 (6.0)	88.1 (6.0)	89.9 (6.0)	91.8 (6.0)	90.9 (6.0)
RT Sulfate	2.99 (.03)	2.97 (.01)	2.94 (.02)	2.81 (.02)	2.79 (.03)
H "	15.8 (.33)	15.4 (.38)	15.3 (.33)	15.2 (.25)	13.8 (.22)
A "	128 (7)	124 (6)	124 (7)	123 (7)	111 (6)
RT Oxalate	4.80 (.06)	4.77 (.04)	4.74 (.04)	4.51 (.05)	– –
H "	1.73 (.04)	1.74 (.03)	1.75 (.04)	1.79 (.06)	– –
A "	25.0 (1.6)	25.3 (1.5)	25.3 (1.5)	26.0 (1.6)	– –

seconds, respectively.

All runs in Tables 26-29 are well within the linear working range of the conductivity detector for all of the anions of interest but this is not true for some runs with high sample HCl or NaOH contents. The linear range for this detector is less than 500 ppm of total anion concentration for a 100 ul injector loop or less than 5000 ppm for a 10 ul injector loop. The 10 ul loop was used here.

Tables 26-27 present results for the chromate-sulfate systems and Table 28-29 for the phosphate-sulfate-oxalate systems. Typical chromatographs are presented for the chromate-sulfate system and the phosphate-sulfate-oxalate system in Figures 1 and 2, respectively. For Tables 26-29, each of the runs represents the same concentration of ions except for varying HCl and NaOH; the first row in these Tables gives the HCl or NaOH concentration used. The zero (0) entry refers to solutions to which no HCl or NaOH were added, and these will be taken as the reference in later disscusions.

The pH and the ionic strength of the other runs vary widely, and the data in Tables 26-29 shows how the results vary with hydrogen and hydroxide ion content.

The symbols HW, k', a and R in Tables 30-37

Figures 1 and 2 follow.

Figure   1. Typical New Chromium Plating Solution

Chromatograph Using An AG4 Column

Peak A: Sulfate

Peak B: Chromate

Figure 1

144b
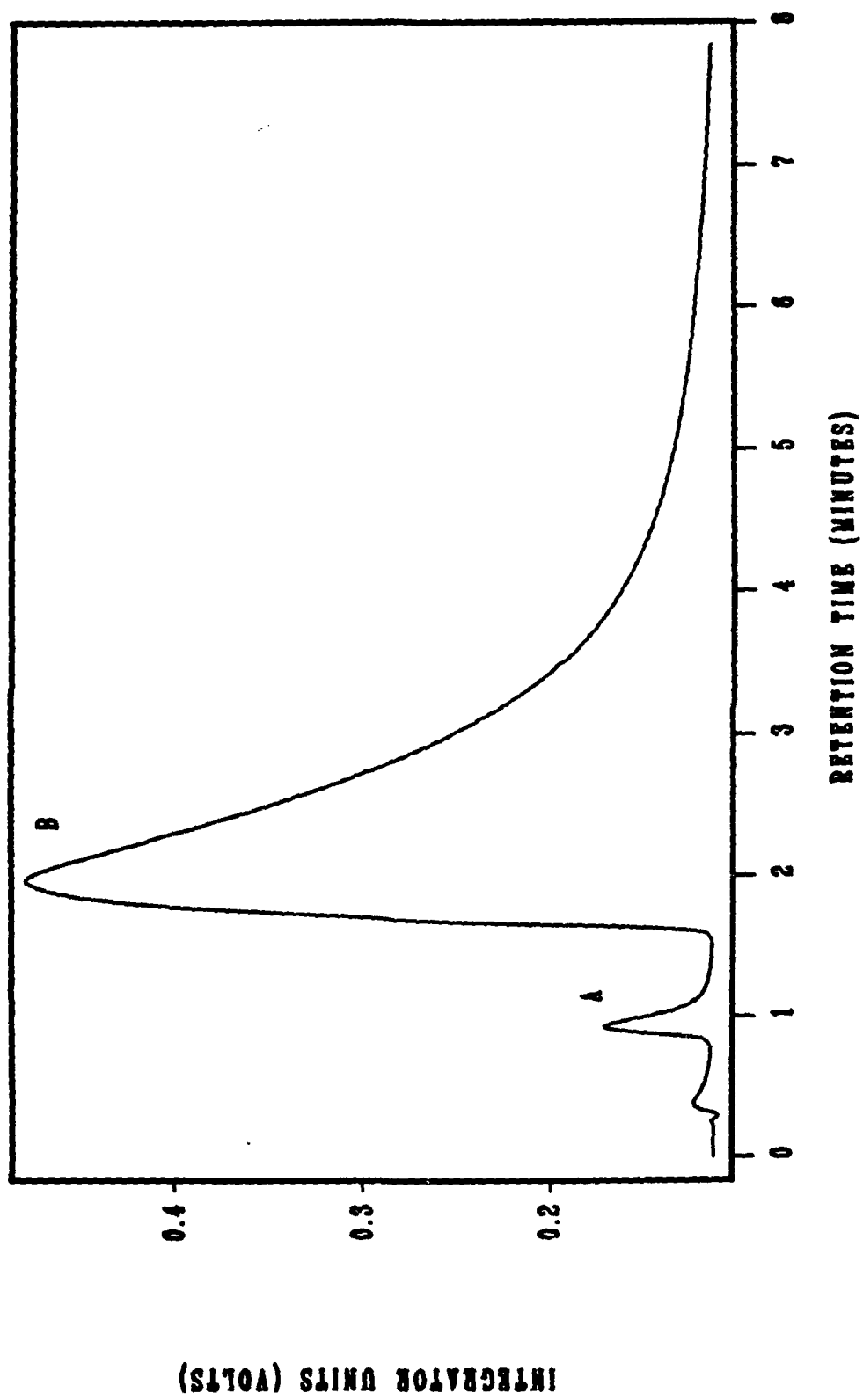
Figure 2. Typical New Acid Treatment Solution

Chromatograph Using An AG4 Column

Peak A: Phosphate

Peak B: Sulfate

Peak C: Oxalate
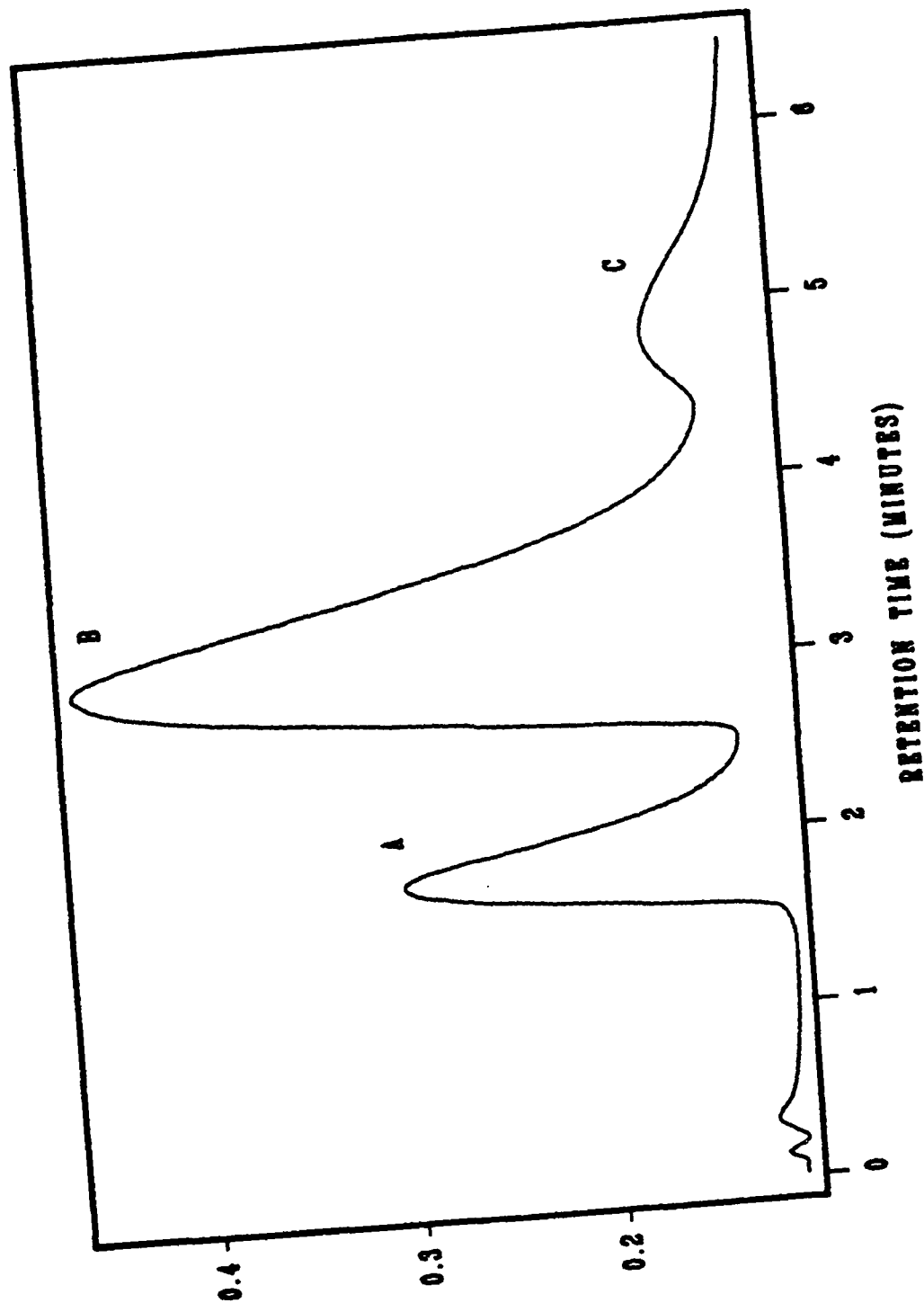
Figure 2

End of Figures 1 and 2.

Table   30. Chromium Plating Solutions k'
and HW (sec) with Added HCl

N HCl	.1	.1	.01	.001	0
k' Chloride	–	1.6	.6	.3	.3
k' Sulfate	–	–	–	1.2	1.2
k' Chromate	–	5.4	4.1	3.7	3.7
RW Chloride	–	66	42	36	6
EW Sulfate	–	–	–	9	9
LW Chromate	–	27	24	24	24

chloride from sample chromate

Table   31. Chromium Plating Solutions k'

and HW (sec) with Added NaOH

N NaOH	0	.001	.01	.1	1
k' Hydroxide	.3	.3	.3	.3	.3
k' Sulfate	1.2	1.2	1.2	1.2	-
k' Chromate	3.7	3.7	3.5	3.4	3.4
RW Hydroxide	6	6	6	6	30
EW Sulfate	9	9	9	9	-
LW Chromate	24	24	24	24	21

hydroxide from sample chromate

Table   32. Acid Treatment Solutions k'

and HW (sec) with Added HCl

N HCl	1	.1	.01	.001	0
k' Chloride	–	3.1	1.2	.6	.6
k' Phosphate	–	–	3.2	3.2	3.2
k' Sulfate	–	6.4	6.1	6.1	6.1
k' Oxalate	–	–	10.4	10.4	10.4
RW Chloride	–	51	30	24	6
EW Phosphate	–	–	21	18	18
EW Sulfate	–	33	33	30	30
LW Oxalate	–	–	36	30	30

chloride from sample phosphate and sulfate

Table 33. Acid Treatment Solutions k'

and HW (sec) with Added NaOH

N NaOH	0	.001	.01	.1	1
k' Hydroxide	.6	.6	.6	.6	1.1
k' Phosphate	3.2	3.2	3.1	3.0	3.0
k' Sulfate	6.1	6.1	6.0	5.7	5.6
k' Oxalate	10.4	10.3	10.3	9.7	-
RW Hydroxide	6	6	6	6	15
EW Phosphate	18	18	18	18	18
EW Sulfate	30	30	30	30	30
LW Oxalate	30	30	30	27	-

hydroxide from sample phosphate and sulfate

Table 34. Chromium Plating Solutions

a and R with Added HCl

N HCl	1	.1	.01	.001	0
a Sulfate/Chloride	–	–	–	4.0	4.0
a Chromate/Chloride	–	3.4	6.8	12.3	12.3
a Chromate/Sulfate	–	–	–	3.1	3.1
R Sulfate/Chloride	–	–	–	.51	1.5
R Chromate/Chloride	–	1.0	1.3	(sulfate present)	
R Chromate/Sulfate	–	–	–	1.5	1.5

Table 35. Chromium Plating Solutions

a and R with Added NaOH

N	NaOH	0	.001	.01	.1	1
a	Sulfate/ Hydroxide	4.0	4.0	4.0	4.0	-
a	Chromate/ Hydroxide	12.3	12.3	11.7	11.3	11.3
a	Chromate/ Sulfate	3.1	3.1	2.9	2.8	-
R	Sulfate/ Hydroxide	1.5	1.5	1.5	1.5	-
R	Chromate/ Hydroxide	(	sulfate	present	)	1.5
R	Chromate/ Sulfate	1.5	1.5	1.5	1.5	-

Table 36. Acid Treatment Solutions
a and R with Added HCl

N HCl	1	.1	.01	.001	0
a Phosphate/ Chloride	-	-	2.7	5.3	5.3
a Sulfate/ Chloride	-	2.1	5.1	10.2	10.2
a Oxalate/ Chloride	-	-	8.7	17.3	17.3
a Sulfate/ Phosphate	-	-	1.9	1.9	1.9
a Oxalate/ Sulfate	-	-	1.7	1.7	1.7
R Phosphate/ Chloride	-	-	1.0	1.6	2.8
R Sulfate/ Chloride	-	1.0	(phosphate present)		
R Sulfate/ Phosphate	-	-	1.3	1.5	1.5
R Oxalate/ Sulfate	-	-	1.6	1.8	1.8

Table 37. Acid Treatment Solutions

a and R with Added NaOH

N NaOH	0	.001	.01	.1	1
a Phosphate/ Hydroxide	5.3	5.3	5.2	5.0	2.7
a Sulfate/ Hydroxide	10.2	10.2	10.0	9.5	5.1
a Oxalate/ Hydroxide	17.3	17.2	17.2	16.2	-
a Sulfate/ Phosphate	1.9	1.9	1.9	1.9	1.9
a Oxalate/ Sulfate	1.7	1.7	1.7	1.7	-
R Phosphate/ Hydroxide	2.8	2.8	2.6	2.5	1.5
R Sulfate/ Hydroxide	(	phosphate present			)
R Sulfate/ Phosphate	1.5	1.5	1.5	1.4	1.4
R Oxalate/ Sulfate	1.8	1.8	1.8	1.8	-

represent the same quantities as used earlier and again
they illustrate the quality of the chromatography.
Cations are in the NRP's.

Injected sulfuric and chromic acid concentrations
of all samples in Tables 26-27 are identical as
described in the experimental section. The chromic
acid concentration is at the threshold of overloading
the low capacity of the column in order to analyze
trace sulfuric acid in the same run. As a result, the
chromate peak has lost its guassian peak shape in favor
of a shape with moderate tailing.

The effect of acidity is shown in Table 26. Due
to the HCl present in the samples, the following
equilibria exist before injection:

$$Cr_2O_7^{2-} \longleftrightarrow 2CrO_4^{2-} + 2H^+ \tag{68}$$

$$HSO_4^- \longleftrightarrow SO_4^{2-} + H^+ \tag{69}$$
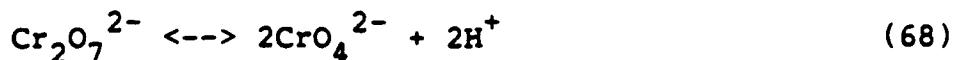
$$Ka' = (CrO_4^{2-})^2(H^+)^2/$$
$$(Cr_2O_7^{2-}) = 3.2x10^{-7} \tag{70}$$

$$Ka' = (H^+)(SO_4^{2-})/(HSO4^-) = 1.2x10^{-2} \tag{71}$$

The pKa' for chromate/ dichromate is 6.50 and the pKa'
for sulfate is 1.92. The pKa' for both chromate/
dichromate and sulfate is too low in value to be
considered here. Under acid conditions, an
intermediate step in the chromate/ dichromate
conversion is:

$$2(HCrO_4^-) \longleftrightarrow Cr_2O_7^{2-} + H_2O \tag{72}$$
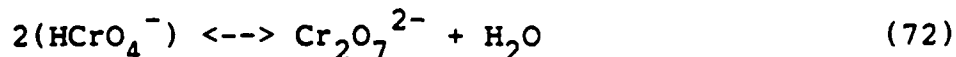
Substitution into equation 70 of Ka' and hydrogen ion concentration, for the chromate/ dichromate system gives the ratio of more dissociated to less dissociated species at a given pH as Table 38 shows.

From pH= 8-14, the chromium is at least 99% in the chromate form. At pH= pKa'= 6.50, the square of the hydrogen ion concentration is Ka'= 0.00032 mM and the ratio of the two species is one. The analogous data for sulfate are in Table 39.

From pH= 4-14, the sulfur is at least 99% sulfate. At pH= pKa'= 1.92, the hydrogen ion concentration equals Ka'= 0.012 M and the ratio of sulfate to bisulfate is one.

The measured pH of .003 M sodium carbonate eluent used for chromate runs is 10.35. The measured pH for a 250 dilution of chromium plating solution standard from above is 2.42. The measured pH of a 1:1 mixture of these two solutions is 2.89. When hydrogen ion is added to the sample, the sample acid becomes less dissociated before injection. Sample hydrogen ions lowers the pH below the normal 2.4-2.5 region. The opposite takes place when hydroxide ions are added.

From the time of injection, regardless of what sample hydrogen or hydroxide ion concentrations that

Table 38. Ionic Ratios in Chromate/ Dichromate

Solutions as a Function of pH

pH	log (Chromate)(Chromate)/(Dichromate)
1	-4.49
2	-3.49
3	-2.49
4	-1.49
5	-0.49
6	0.51
7	1.51
8	2.51
9	3.51
10	4.51
11	5.51
12	6.51
13	7.51
14	8.51

Table 39. Ionic Ratios in Sulfate

Solutions as a Function of pH

pH	log (Sulfate)/(Bisulfate)
1	-0.16
2	0.84
3	1.84
4	2.84
5	3.84
6	4.84
7	5.84
8	6.84
9	7.84
10	8.84
11	9.84
12	10.84
13	11.84
14	12.84

were present in the original sample, the sample acids become progressively more dissociated due to the basic carbonate eluent at a normal pH of 10.35. Unreacted hydrogen or hydroxide ions from the sample reacts with the eluent, shifting the carbonate/ bicarbonate equilibrium as shown above. The change in carbonate molarity due to the addition of sample HCl or NaOH is difficult to predict.

In the eluent ranges used, a linear ion exchange mechanism exists where the retention time is inversely proportional to the carbonate concentration. This is derived from the van Deepter equation.

Unsymmetric peaks result when a high concentration ion elutes in the void volume while a low concentration ion is mildly retained. It is better to have the low concentration ion mildly retained and the high concentration ion more strongly retained (73). No change in retention time indicates that the column capacity was not exceeded. Dilution gives better resolution of peaks but lower precision (22). If marginal baseline resolution is present, quantitative results require spiking or standard additions.

In Table 26, the sulfate in samples that contained 1 N, .1 N and .01 N HCl was totally hidden within the large chloride peak. The sulfate sample containing

.001 N HCl was partially masked due to its close
proximity to the chloride peak. Since the sulfate
retention time is not much longer than that of
chloride, small amounts of chloride affect the sulfate
peak. If bisulfate exists, even for a short time in
the column, it will broaden the sulfate band on the
chloride side and this broadened area will be lost in
the chloride peak.

If a peak shows an abrupt change in its shape,
this may be due to another small peak within that peak.
This is especially true if a preceeding or following
tail is seen for the peak shape. An example of this
occurs when dichromate and chromate are present giving
a situation of band broadening.

Similarly, the chromate in the sample containing
1 N HCl was totally lost witnin the big chloride peak.
The chromate in samples containing .1 and .01 N HCl was
partially covered by the chloride peak, but the .001 N
HCl containing sample was not affected by chloride and
gave the same results as a run which lacks chloride.

One factor that contributes to increasing chromate
retention times as sample HCl concentration increases
is due to sample dichromate having a higher affinity
for the column resin than chromate, which leads to
band broadening on the high retention time side of the

chromate peak (27). This results even if the dichromate is reconverted to chromate after a short time on the column. This band broadening increases chromate retention times as acid concentration increases.

A second factor that contributes to increasing chromate retention times as chloride concentration increases is due to the chloride ion having much less affinity for the column resin than the chromate ion. As a result, the chloride band must elute before the chromate band due to the principles of displacement chromatography. Diplacement chromatography is when a large concentration of one species "pushes" a large concentration of another species down the column, assisting the eluent (10). Unfortunately, the chromate samples containing .1 N and .01 N HCl lost a significant portion of their bands within the relatively large preceding chloride band. Since the chloride and chromate bands are not totally resolved, an overlap exists between the two bands and this increases chromate retention times as chloride concentration increases. Due to chromate band loss in the chloride band, chromate peak height and apparent area decreases. As chromate retention time increases, chromate peak height decreases.

A final factor that contributes to increasing chromate retention times as HCl concentration increases is due to the sample protons that do not react to form dichromate. This excess only exists in samples containing 1 N, .1 N and possibly .01 N HCl. This unreacted sample HCl always shifts the carbonate-bicarbonate equilibria in favor of bicarbonate (10):

$$\text{acid + carbonate} \longrightarrow \text{bicarbonate} \qquad (73)$$

The measured pH of the sodium carbonate eluent is about 10.8 in all cases and thus there is about three times more carbonate than bicarbonate. Since the bicarbonate is a weaker eluent than the carbonate ion, this causes a weakened eluent zone around the initial chromate band, that contributes to longer chromate retention times and decreased peak heights. This effect will diminish as HCl is neutralized by the new eluent and the extra bicarbonate is carried down the column faster than the sample anions. Highly retained anions such as chromate and oxalate are more affected by local eluent changes from sample HCl than are moderately retained anions such as phosphate and sulfate.

Due to the HCl present in the samples, the following equilibria exist before injection:

$$\text{bicarbonate} \longleftrightarrow \text{carbonate + acid} \qquad (74)$$

$$Ka' = (H^+)(CO_3^{2-})/(HCO_3^-) = 4.8 \times 10^{-11} \qquad (75)$$

The pKa' for carbonate is 10.32. The pKa for carbonate is too low in value to be considered here. Substitution into equation 75 of the Ka' and the hydrogen ion concentration values for carbonate gives the ratio of more dissociated to less dissociated species at a given pH as Table 40 shows.

A change of one pH unit changes the above eluent ratio by a factor of ten and this has a significant effect on retention time and peak height. From pH= 13-14, the species is at least 99% carbonate. At pH= pKa'= 10.32, the hydrogen ion concentration equals Ka'= 0.000048 micro-molar and the ratio is one.

It should be noted that the chloride ion is about as good a "pusher" ion as bicarbonate and should contribute to reduced chromate retention times but this affect is overcome by the countering affects previously mentioned.

There is an instrumental, computational factor that contributes to decreasing chromate peak areas for samples containing .1 and .01 N HCl and is due to the way the integrator calculates the end of a tailing peak. The integrator "decides" the end of a tailing peak when the slope of the tail drops below a certain value for a certain amount of time. If a set of

Table 40. Ionic Ratios in Carbonate

Solutions as a Function of pH

pH	log (Carbonate)/(Bicarbonate)
1	-9.32
2	-8.32
3	-7.32
4	-6.32
5	-5.32
6	-4.32
7	-3.32
8	-2.32
9	-1.32
10	-0.32
11	0.68
12	1.68
13	2.68
14	3.68

samples are run that all have different degrees of tailing, then the areas can only be semi-quantitatively compared.

For chromate with its initial non-gaussian, tailing character, the tailing increases with increased sample chloride concentration. The integrator ends the various degrees of tailing peaks at the same slope. Even though chromate peak areas are constant, the integrator will report a larger chromate area for a sample with no HCl compared to one with HCl present. This accounts for all the differences in area as related to the Tables. Manual integration of these peaks also suffers from uncertainty as to where the tail actually merges with the baseline.

As mentioned, a low capacity column is operated at the threshold of overloading and additional chloride overloads the column capacity, resulting in non-gaussian peak shapes. The number of effective ion exchange sites or theoretical plates (N) is reduced for chromate. Thus, a change in N is related to changing the RT, H, and A from equations 12-13. The affect of N on RT, H, and A is shown in the experimental data of Table 26 since N is inversely proportional to increasing sample chloride concentration.

In Table 27, the effect of sample sodium hydroxide is studied as it relates to retention time, peak height and peak area for sulfuric and chromic acids. The sample hydroxide does not react with the sulfate or chromate ions before or after injection.

Regeneration of hydroxide produces a water dip on the chromatograph that is large at high hydroxide concentrations. With 1 M NaOH, the sulfate peak is totally lost within this dip, while with 0.1 M NaOH, a small loss of the sulfate peak was seen but the retention time was effected. Other hydroxide concentrations had no effect. Similarly, the chromate was obscured by the water dip when 1 M NaOH was present, but because of the larger retention time compared to sulfate, the other concentrations of base did not effect this peak.

One factor that contributes to decreasing chromate retention times as hydroxide increases is the hydroxide acting as a "pusher" ion like carbonate and bicarbonate. The order of decreasing "pusher" ion strength is carbonate, bicarbonate, chloride and then hydroxide but at high hydroxide concentrations a mild affect on chromate retention time is present. With the low capacity column at the overload threshold, the extra sample hydroxide overloads the column capacity

and effectively reduces the number of ion exchange sites available to chromate as hydroxide concentration increases. This reduces chromate retention times while increasing peak heights.

Another factor that contributes to decreasing chromate retention times as hydroxide concentration increases is the unreacted sample NaOH that shifts the eluent carbonate-bicarbonate equilibria in favor of carbonate (10):

hydroxide + bicarbonate --> carbonate + water (76)

Since carbonate is a stronger "pusher" ion than the bicarbonate, the eluent is strengthened. At the eluent pH, the carbonate-bicarbonate concentration ratio is about 3, and carbonate conversion only has a mild affect on chromate retention times as the data illustrates. If additional carbonate is formed around the sample band, even for a short period of time, it will contribute to shorter chromate retention times and increased peak heights. This effect will also diminish as NaOH is neutralized by the new eluent and the extra carbonate is carried down the column faster than the sample anions. Highly retained anions such as chromate and oxalate are more affected by local eluent changes from sample NaOH than are moderately retained anions such as phosphate and sulfate.

It is suspected that the decreased chromate retention times result from a combined "pushing" effect from direct hydroxide ion and indirect carbonate conversion from hydroxide.

The mild increase in chromate peak area for samples containing .1 N, .01 N and .001 N NaOH is again attributed to the way the integrator calculates the end of a tailing peak. For chromate with its initial non-gaussian, tailing character, the tailing decreases with increased sample hydroxide concentrations. The integrator ends the various degrees of tailing peaks at the same slope. Even though actual chromate peak areas may be constant, the integrator will report a smaller chromate area for a sample with no hydroxide compared to one with hydroxide present.

Overloading of hydroxide has the same affect on the chromate band as chloride overloading had above. This affect again reduces the effective ion exchange sites (N) for chromate thus affecting RT, H and A. The affect of N on RT, H, and A is shown in the experimental data of the Tables since N is inversely proportional to increasing sample hydroxide concentrations.

The injected phosphoric, sulfuric and oxalic acid concentrations of all runs in Tables 28-29 are

identical as described in the Experimental section. The combined concentrations of the phosphoric and sulfuric acids are at the threshold of overloading the low capacity column in order to analyze trace oxalic acid in the same run. As a result, the phosphoric and sulfuric acid peaks have slightly lost their gaussian peak shapes in favor of shapes with slight tailing.

In Table 28, the effect of sample HCl is studied as it relates to retention time, peak height and peak area for phosphoric, sulfuric and oxalic acids. The concentrations of the sample HCl used were the same as Table 26.

Due to the HCl present in the samples, the following equilibria exist before injection:

$$\text{pyrophosphate} \longleftrightarrow \text{biphosphate} + \text{acid} \qquad (77)$$

$$\text{biphosphate} \longleftrightarrow \text{phosphate} + \text{acid} \qquad (78)$$

$$\text{bisulfate} \longleftrightarrow \text{sulfate} + \text{acid} \qquad (79)$$

$$\text{bioxalate} \longleftrightarrow \text{oxalate} + \text{acid} \qquad (80)$$

$$Ka' = (H^+)(HPO_4^{2-})/(H_2PO_4^-) = 6.2 \times 10^{-8} \qquad (81)$$

$$Ka'' = (H^+)(PO_4^{3-})/(HPO_4^{2-}) = 4.8 \times 10^{-13} \qquad (82)$$

$$Ka' = (H^+)(C_2O_4^{2-})/(HC_2O_4^-) = 5.1 \times 10^{-10} \qquad (83)$$

The pKa' for phosphate is 7.21, the pKa'' for phosphate is 12.32 and the pKa' for oxalate is 9.29. The pKa's for both phosphate and oxalate are too low in value to be considered here.

Substitution into equations 81 and 82 of the Ka',
Ka'' and the hydrogen ion concentration values for
phosphate gives the ratio of more dissociated to less
dissociated species at a given pH as Table 41 shows.

From pH= 10, the species is at least 99%
biphosphate. At pH= pKa'= 7.21, the hydrogen ion
concentration equals Ka'= 0.0000617 mM and the first
ratio is one. At pH= pKa'= 12.32, the hydrogen ion
concentration equals Ka'= 0.000000479 micro-molar and
the second ratio is also one.

Substitution into the equation 83 of the Ka' and
the hydrogen ion concentration values for oxalate gives
the ratio of more dissociated to less dissociated
species at a given pH as Table 42 shows. From pH=
12-14, the species is at least 99% oxalate. At pH=
pKa'= 9.29, the hydrogen ion concentration equals Ka'=
0.00051 micro-molar and the ratio is one.

The measured pH of .001 M sodium carbonate eluent
used for acid runs is 9.96. The measured pH for a 250
dilution of acid solution standard from above is 2.54.
The measured pH of a 1:1 mixture of these two solutions
is 2.72. When hydrogen ions are added to the sample
volumetric flask, the sample acid becomes less
dissociated in that flask before injection. Sample
hydrogen ions lower the pH below the normal 2.4-2.5

Table 41.   Ionic Ratios in Phosphate
Solutions as a Function of pH

pH	log (Biphosphate)/ (Pyrophosphate)	log (Phosphate)/ (Biphosphate)
1	-6.21	-11.32
2	-5.21	-10.32
3	-4.21	- 9.32
4	-3.21	- 8.32
5	-2.21	- 7.32
6	-1.21	- 6.32
7	-0.21	- 5.32
8	0.79	- 4.32
9	1.79	- 3.32
10	2.79	- 2.32
11	3.79	- 1.32
12	4.79	- 0.32
13	5.79	0.68
14	6.79	1.68

Table 42. Ionic Ratios in Oxalate

Solutions as a Function of pH

pH	log (Oxalate)/(Bioxalate)
1	-8.29
2	-7.29
3	-6.29
4	-5.29
5	-4.29
6	-3.29
7	-2.29
8	-1.29
9	-0.29
10	0.71
11	1.71
12	2.71
13	4.71
14	4.71

region.

When hydroxide is added to the sample volumetric flask, the sample acid becomes more dissociated in that flask before injection. Sample hydroxide raises the pH above the normal 2.4-2.5 region.

From the time of injection, regardless what sample hydrogen and hydroxide ion concentrations were present initially, the sample acids become progressively more dissociated due to the basic carbonate eluent at a normal $pH= 9.96$. Unreacted hydrogen and hydroxide ions from the sample react with the eluent, shifting the carbonate/ bicarbonate equilibrium as shown above.

The behavior of sulfate in this system is exactly the same as in previous discussions. Phosphate and oxalate behave in analogous ways for the same reasons. Loss of peaks in high acid concentrations is due to masking by the large chloride peak, while disappearances at high base concentrations arise from interferences by the water dip. Changes in the retention times and band shapes result from changes in acid-base equilibria on the column at high acid or base concentrations, as well as interferences with adsorption sites as discussed above. Peak area changes result in part from behavior of the integrator.

There are some literature reports of trace a

but not with higher level solution anions, being masked or affected by extreme column overload which affects retention times and heights (12, 14, 27, 30, 33, 46, 47, 73). In this report, it is seen that extreme column overload is not necessary to affect the quantitative results of the trace as well as the higher concentration solution anions. It is further illustrated here that eluent pH, equilibrium and strength can be affected by sample pH and ionic concentrations.

The AG4 column overloads at greater than a 1000 ppm anion concentration with a 10 uL loop. Quantitative analysis is possible on an overloaded column if standards and samples have the same pH/ concentrations and are made up from the same acids/ salts. Appropriate further dilution could quantify the major anions, but this would make the minor anions undetectable.

Runs that contain no HCl or NaOH had the standard eluent controlling elution for the entire run. This resulted in peaks that rose slightly faster than they returned to baseline and as they returned to the baseline there was moderate tailing. Reference runs in Tables 26-29 exhibit these moderately non-gaussian characteristics. Runs that contained HCl started with

a locally weaker eluent that resulted in band broadening, lower peak heights, longer retention times, more tailing, and excessively non-gaussian characteristics compared to the reference runs. Runs that contained NaOH started with a locally stronger eluent and showed the opposite behavior; that is, band narrowing, higher peak heights, shorter retention times, less tailing, and only mildly non-gaussian characteristics compared to the reference runs. These changes in peak shape are significant for the analytical response.

The reasoning that the HCl or NaOH, respectively, is responsible for the variations is supported since the chromate peak gives the same results on the uv-visible and A.A. online detectors which lack the chemical suppressor column. This confines the effect to the eluent, separator column, and sample and thus it is not detector related. Interferences from other ions were excluded since other eluent strengths gave the same relative results with the same relative peak shapes indicating no interference (2). Furthermore, AA detectors in particular are specific for chromium. Standards/ samples must have the same counter-ions and acid-base characteristics for quantitative results. If standards and samples are made of different counter-

ions, error may result in the analysis depending on concentrations and pH. In Tables 26-29, the chromate and the oxalate peak heights are most affected by eluent changes due to sample HCl or NaOH since they are highly retained anions. Similar errors are present, but less severe for moderately retained anions in both systems.

If the equivalent amount of chromate as sodium chromate instead of chromic acid is used in the reference runs of Tables 26-27, then that would be the same as neutralizing the chromic acid in the reference run with .014 M NaOH. This includes the very minimal effect of sulfuric acid present. The results lie where they are expected in Table 27. The parallel argument is valid for potassium chromate salts also. In a similar way, if the equivalent amount of oxalate as sodium oxalate or potassium oxalate instead of oxalic acid is used in the reference runs of Tables 28-29, that would be the same as neutralizing the phosphoric, sulphuric and oxalic acids present with 0.0128 M NaOH or KOH. The results also lie where they are expected in Table 29. The results are that significant error occurs in the chromate and oxalate heights when standards and samples are not both made to have the same acid or base content.

The difference in behavior between solutions made from chromic acid and from chromate salt is illustrated by the RT and H values of 1.96 minutes and 8.82 uS for chromic acid, but 1.84 minutes and 11.3 uS for sodium chromate. The acid solution had a water dip and the chromate peak had extreme band broadening, while the salt solution had no water dip and its chromate peak had only mild band broadening. Thus, the water dip is eliminated by eluent dilution or by using the sodium salt for chromate.

For chromate, ACS certified chromic acid and potassium chromate are free of chloride and sulfate and a 250 dilution of the plating solution gives good sulfate and chromate resolution (27). The chromate results agree with titration method data.

Highly polarizable ions such as chromate are retained on the column by: 1) ion exchange 2) normal activity adsorption sites 3) much higher activity adsorption sites. The last of these causes chromate peak tailing. Acetonitrile and para-cyano-phenol at low eluent concentrations will minimize tailing of the chromate by blocking these strongly active adsorption sites (73). The chromate tailing is minimized when the chromate eluent contains 0.71 mM para-cyano-phenol and 3% v/v acetonitrile which is the maximium allowed value

for this column. This is proof that the chromate
tailing is partly due to very active adsorption sites.

From above, weakening and strengthing of the
eluent is what changes the retention times of the
chromate but the peak profiles (broadening, tailing,
etc.) are also changed since the weaker and stronger
eluents have different "exchange" rates on the ion
exchange sites and the adsorption sites. Also, as the
sample load is increased the oxalate and chromate
tailing decreases since active adsorption sites are
"saturated". The percentage of solute molecules
affected becomes low and the tail is less noticeable.
Also, as the sample load increases, the retention time
decreases and tailing decreases as shown in Table 43.

Conductance (G) was calculated by equation 49 for
10 ppm of each of the anions in Table 44 for the acid
and sodium salt forms, and E was from Table 3. The
results are presented for common anions in Table 44.
Calculated G values, in uS, are utilized for a
retention time of 1 second which is a function of
height for any given anion. Since RT is inversely
proportional to height, at about y seconds, the height
H= G/y uS. This value at 10 ppm compares well with the
measured values in Tables 26-29. For example, the
calulated G for sulfuric acid was 1.1 uS and the

Table 43. Chromatographic Effects of Sample Load
on Chromium Plating and Acid Treatment Solutions

Species	Conc (ppm)	RT (min)	H (uS)
Sulfate	3.3	.96	.44
"	6.7	.93	.71
"	10.0	.92	1.18
Chromate	333.	2.60	3.60
"	667.	2.25	5.56
"	1000.	1.96	8.82
Phosphate	92.	1.96	4.1
"	184.	1.82	7.7
"	288.	1.78	10.4
Sulfate	118.	3.36	7.9
"	235.	3.10	12.4
"	353.	2.99	15.8
Oxalate	24.	5.07	.65
"	48.	4.89	1.09
"	72.	4.80	1.73

Table 44. Calculated Conductances for Common Anions

	Acid Form G (uS)	Sodium Form G (uS)
Chloride	130	30
Carbonate	154	20
Sulfate	80	20
Oxalate	80	20
Chromate	80	20
Phosphate	110	20

measured G was 1.2 uS giving good agreement at RT= 70 seconds.

The capacity factor, selectivity and resolution correlate well with the data in Tables 26-29.

As the Dionex AG4 columns ages, the quantitative differences in response with acid or base content increases for the chromate/ sulfate and phosphate/ sulfate/ oxalate systems. These differences exceed those shown here on the same new column for both peak height and area. As the pH is varied by HCl or NaOH, the most retained ions give the greatest deviations. An example of this behavior is the chromiun plating system where the sulfate and chromate retention times are .92 minute and 1.96 minutes for a new AG4 column and .91 minute and 1.81 minutes for an old AG4 column. Another example of this behavior is the acid treatment system where the phosphate, sulfate and oxalate retention times are 1.78 minutes, 2.99 minutes and 4.80 minutes for a new AG4 column; and 1.74 minutes, 2.89 minutes and 4.42 minutes for an old AG4 column. This behavior is caused by irreversibly bound species that alter future runs by lowering anion column performance and by increasing operating pressures. The species include anionic and hydroxide precipitated metal complexes; highly polarizable anions, and oxidizing

species such as nitrite and dichromate (12, 27, 73).

Acceptable quantitative results require accuracy with less than 5% error for any system being analyzed. Quantitation of both anions in Tables 26-27 required less than .001 N HCl and less than .001 N NaOH using the conditions of the reference run as a standard. Quantitation of the 3 anions in Tables 28-29 required less than .001 N HCl and less than .001 N NaOH. Also true is the fact that the old columns are less tolerant of pH variations. They give higher error compared to the new columns under the same conditions. Thus, the allowable pH differences between standard and sample solutions is narrower for quantitative analysis for old compared to new columns. This is attributed to physically or irreversibly bound contaminates that block partitioning sites and lower retention times as is evident when old and new columns are compared for the same systems and conditions.

These results show the necessity for utilizing standards and samples of similar acid-base characteristics when these metal finishing solutions are analyzed by ion chromatography. Also, column life is a factor in quantitative analysis as shown.

4.7.2 Determination of Nitrate and Nitrite

in Metal Finishing Solutions

This is a quick, sensitive, specific, and precise method for the analysis of nitrate and nitrite in metal finishing solutions. A HPIC-AG4 column is used with ion chromatography and suppressed conductivity detection. This method can quantitatively analyze ppm levels of these anions and is more precise than classical methods.

These anions and other anions are retained by the column but the cations are not. This method can be performed online, unlike the classical methods that it replaces.

Table 45 shows the analysis of nitrate in a chromium plating solution. Identical nitrite runs were made but oxidation to nitrate takes place resulting in only nitrate being seen in the Table. Nitrate and nitrite can be detected in the uv at 210nm as an alternate to conductivity detection (74).

The injected sample was a 250 dilution of the above chromium plating standard solution for each run in this Table. The sulfuric acid peaks (10 ppm) were 1.18 uS at .96 min. and the chromic acid peaks (1000 ppm) were 8.82 uS at 2.36 min. with a 10 uL loop

Table 45. Determination of Nitrate

in Chromium Plating Solutions

(ppm)	RT (min.)	H (uS)
1	.76 (.01)	.14 (.01)
2	.76 (.01)	.28 (.01)
3	.76 (.01)	.42 (.01)
5	.76 (.01)	.69 (.02)

and 30 uSFS. When nitrite was run completely alone, the retention time was at .20 minute. Nitrite could be determined in the presense of nitrate by this procedure, but it cannot exist in this solution.

Conductance (G) was calculated by equation 49 for 10 ppm of nitric acid and sodium nitrate with the resulting respective conductances of 80 uS and 10 uS. The E values are from Table 3 and are at a retention time of one second. In the same way as described for an earlier system, the expected value at the detector after 50 seconds (1.6 uS) also agrees well (1.4 uS).

All runs in Table 45 are well within the linear working range of the conductivity detector for the anions of interest as shown above.

The k' value is .84 for nitrate. The half base width in seconds of the non-retained peak and nitrate are 1 and 3, respectively. The resulting resolution for this system is 5.3.

The capacity factor is just within the ideal range but resolution is again good for all runs. Acceptable quantitative results are acheived by the provisions stated above.

4.8 Determination of Ethylene Glycol Degradation Products in Metal Finishing Solutions

Ethylene glycol is an unwanted component of metal finishing solutions arising from cooling system leaks. In these solutions, it is oxidized by chromate to glycolic acid, oxalic acid, then formic acid before it forms carbonic acid as its end product (75, 76, 77). In this process, Cr(VI) is converted to Cr(III). Acid degradation products depend on acid concentration, temperature, metals present, oxygen present, and inhibitors (75). HPICE has more retention for weak organic acids than strong acids, unlike HPIC (76). Presented here is quick, sensitive, specific, and precise method for the analysis of products of ethylene glycol in metal finishing solutions using an HPICE column with ion chromatography and suppressed conductivity detection. This method can quantitatively analyze ppm levels of these acids and is more precise than classical methods.

These acids and other anions are retained by the column but the cations are not. This method can be performed online, unlike the classical methods that it replaces.

Table 46 shows the analysis of ethylene glycol in metal finishing solutions containing chromate, phosphate, and sulfate by ion exclusion chromatography. Table 46 is for chromium plating solutions but the same

Table 46. Ethylene Glycol Degradation Product Results

Species	ppm	RT (min.)	H (uS)
Oxalic Acid	2	7.0 (.2)	.8 (.1)
Glycolic Acid	28	11.7 (.1)	7.3 (.3)
Formic Acid	17	12.8 (.4)	6.0 (.1)

approach was applied to polish solutions with equal success.

Ethylene glycol (50 ppm) was added to the chromium plating solution and was measured in the hour after reaction due to the kinetic nature of this reaction process. There was a very small peak (.1 uS) at 15.3 minutes that might possibly be carbonic acid but this was difficult to investigate in acidic eluent. There is a great deal of carbonic acid liberated and it is reasonable to assume that some is still present even in an acid medium.

The k' values are 14.5, 25.0 and 27.4 for oxalic, glycolic and formic acids, respectively. The sample cations form the non-retained peak. The glycolic/ oxalic and formic/ glycolic acids separation factor values are 1.7 and 1.1, respectively. The half base widths in seconds of oxalic, glycolic and formic acids are 24, 30 and 36, respectively. The resulting resolution values are 5.2 and 1.0 for glycolic/ oxalic and formic/ glycolic acids, respectively.

The capacity factor is in an acceptable HPICE range and resolution is again good for all runs due to good selectivity.

All runs in Table 46 are well within the linear working range of the conductivity detector for the

anions of interest as shown above and acceptable
results are acheived by the provisions stated above.

4.9 Automated and Online Analysis
of Metal Finishing Solutions

An online and automated system is one that
samples, dilutes, and analyzes its samples with little
to no analyst interaction except to replenish needed
standard solutions and eluents as well as to maintain
the system as needed. This system can be used to
automate all the methods above for high volume quality
control analysis.

Automation modules used were: the autosampler, the
AI-100 programmable controller, and the SP4270 computer/
integrator. These modules gave the ion chromatograph
its online and automated character (78). Inject/ load,
eluent select, pump flow rate, regenerate flow, column
switching, fiber suppressor, extra valves, autozero,
detector settings, attenuation, and start/ end are all
controller programmable. The computer/ integrator
does total data reduction (78). MPIC, HPIC, and HPICE
automation is possible (78). The integrator can
sequentially run up to nine methods that it will switch
by run number. This requires basic patch code data

that switches the files at appropriate points in the program (78).

The k', a, HW and R calculations were already done above in section 4.7.1. The dilution module decreases analyst handling, thus minimizing contamination, preparation time, and variation between analysts (79). By automated or online dilution, ppm or lower analysis is possible and is more precise than classical methods.

Table 47 shows the automated analysis of metal finishing solutions containing chromate, phosphate, and sulfate by ion chromatography using the conditions of section 4.7.1.

Each run in the Table is an average of 40 runs and the standards have been diluted 250 times. Runs 1 and 2 are chromium plating solutions and runs 3 and 4 are polish solutions.

As would be expected, the error in precision or relative standard deviation is higher for low concentration species like 10 ppm sulfuric acid than it is for the other chemical species present. Clearly, the variation in the automated results is acceptably small. The error was calculated from all the data and is lower for any given region of the 40 runs of data. Thus, this error is not random and reflects a

Table 47. Precision of an Automated System

Run	Species	ppm	Average (uS)	S.D. (uS)	R.S.D. (percent)
1	Sulfate	10	1.16	.04	3.4
2	Chromate	1000	8.75	.17	1.9
3	Phosphate	288	10.5	.21	2.0
4	Sulfate	353	16.2	.25	1.5

general trend, which can be related to column aging as discussed in section 4.7.1. This last point is important when standards and samples are alternated in the usual analysis fashion. If the concentrations are calculated only from the previous standard, there will be a smaller error than if all earlier standard peaks are used.

Acceptable quantitative results are acheived by the provisions stated above.

PART 5

CONCLUSION

The procedures discussed in the previous sections offer significant improvements in the analysis of metal finishing solutions. The majority of the procedures are new, and provide major savings in time and reduction of analyst intervention compared to traditional wet chemical methods. The time savings may be very great, for example, these procedures can be carried out in an hour while wet methods may take two days for some chemical species. In addition, sensitivity is improved, especially when it is necessary to determine trace ions in the presence of high concentrations of other ions. Another advantage

is automated, multi-ion determinations.

The precision and specificity are at least as good as in wet chemical methods.

The atomic absorption detector methods, are the methods of choice for metals in the laboratory situation and provide unambiguous identification and specificity while the conductivity and visible detector methods are suitable for the industrial environment as well as the laboratory.

The major disadvantage is the problem that arises from significant differences in sample and standard compositions such as in acidity. This requires caution that standards are made up to closely resemble the analyte sample in overall composition, particularly in regard to high concentration components that may influence the equilibria on which the technique depends. One must always be alert for unanticipated variations of this sort (e.g., in acid or base content) and for this reason wet chemical analysis must still be employed as a check whenever the procedure is applied to samples from an unfamiliar source. The discussions in the sections above have clearly established the potential magnitude of this problem in established procedures in which it has not been previously mentioned.

Three years of testing on real industrial samples, supported by comfirming wet chemical procedures, have shown that these methods work very well. They represent a very significant advance in the analytical techniques available to metal finishing analysts.

PART 6

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